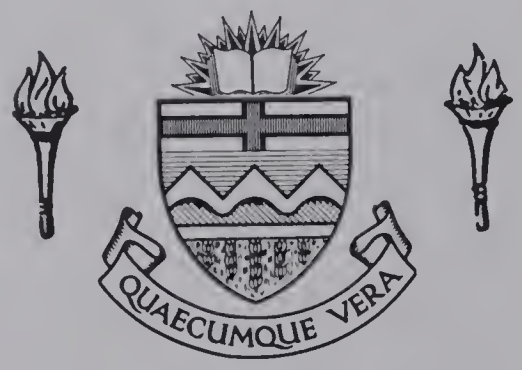
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SULPHUR ISOTOPE EXCHANGE REACTIONS

BY

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A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled SULPHUR ISOTOPE EXCHANGE REACTIONS, submitted by Sheikh Ansar Husain in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

In this thesis, a number of sulphur isotope exchange reactions have been examined for two purposes;

1) to see if exchange occurs, and if so, measure its rate.

2) to determine isotopic equilibrium exchange constants.

The technique was that of having one component in dominant concentration (so that its isotopic composition remained essentially unaltered) and monitoring the $^{34}S/^{32}S$ composition of a minor component as a function of time. From the isotopic composition versus time curves of the minor component, half times for the exchange could be derived and the isotopic equilibrium constant determined by direct examination or by calculations based on the partial exchange technique of Northrop and Clayton (1966). The results can be summarized as follows:

SO_2 was found to exchange with 96% H_2SO_4, solid Na_2SO_4 and Na_2SO_4 solution. In the $H_2SO_4 \leftrightarrow SO_2$ studies the exchange rate was directly proportional to SO_2 pressure but alteration of O_2 pressure had no noticeable effect. The equilibrium constants derived, agreed with those found by Dunford et al (1957) and theoretical calculations.

SO_2 was found to exchange with $NaHSO_3$ solution at 21°C and 80°C. The equilibrium constants found were lower than those obtained by Thode et al (1945).

Exchanges involving H_2S and SO_2 with $Na_2S_2O_3$ (solution) were complicated by the formation of elemental sulphur. The isotopic composition of the H_2S and SO_2 were altered significantly.

When H_2S was equilibrated with H_2SO_4, the H_2S disappeared. Sulphur, whose $^{34}S/^{32}S$ composition was close to the H_2S, was precipitated and the SO_2 which formed, was about 20 ‰ depleted in ^{34}S with respect to the sulphuric acid.

Elemental sulphur left in contact with H_2SO_4, Na_2SO_4, Na_2SO_3 and $Na_2S_2O_3$ solutions did not alter significantly in its $^{34}S/^{32}S$ abundance ratio.

Where it seemed appropriate, the results were related to natural $^{34}S/^{32}S$ variations.

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CHAPTER I

INTRODUCTION

DISCOVERY OF ISOTOPES AND THEIR MEASUREMENT:

During the early part of this century intensive investigations of radioactivity revealed that certain radioactive atoms were chemically similar to other known species. For example, Boltwood (1906) reported the existance of "IONIUM" which was chemically identical to thorium. Soddy (1910) examined other cases and named those species of atoms which were chemically similar but different in their radioactive properties, "ISOTOPES". In fact, isotopes are different nuclear forms of the same element and occupy the same place in the periodic classification of elements. Using his positive ray parabola apparatus, Thomson (1914) first demonstrated the presence of isotopes for elements of lower atomic weight. He identified two of the three stable isotopes of neon, ^{20}Ne and ^{22}Ne.

Aston (1919-21) and Dempster (1918-22) with their mass spectrographs made isotopic abundance determinations of a large number of elements. King and Birge (1929), Giauque and Johnston (1929), Naude (1930) and Urey et al (1931) utilized conventional optical spectroscopy to identify isotopes of the elements carbon, nitrogen and oxygen. In recent years instrumentation has been refined so that:

(i) nuclidic masses can be determined to eight significant figures.

(ii) differences in isotopic abundance ratios of less than 0.01 per cent can be reproducibly measured.

(iii) samples of less than 1 μg can be analyzed isotopically.

EQUILIBRIUM ISOTOPE EFFECTS:

Failure of initial attempts to obtain a separation of isotopes by chemical means led to the belief that isotopes of an element were chemically similar. This concept was abandoned with the discovery of deuterium by Urey et al (1931). Since deuterium has twice the mass of protium, it seemed quite unreasonable that hydrogen isotopes should be identical in their chemical behaviour.

Rittenberg and Urey (1934) made theoretical calculations based on statistical mechanics for the equilibrium constants at different temperatures for the exchange reaction:

$$H_2 + D_2 \rightleftharpoons 2\ HD$$

The equilibrium constants were found to differ from unity indicating differences in chemical behaviour of the hydrogen isotopes. Farkas and Farkas (1934) made similar calculations

for the hydrogen-water exchange reaction. There was quite a good agreement between theoretical predictions and the experimental results. The calculations of Urey and Grieff (1935) for isotopic exchange of many of the lighter elements (boron, carbon, nitrogen, oxygen and chlorine) predicted equilibrium isotope effects of as high as 10 per cent for reactions involving isotopes of these elements. Data for many equilibrium isotope exchange reactions were summarized by Urey (1947).

KINETIC ISOTOPE EFFECTS:

Following the discovery of deuterium, investigators carried out experiments which demonstrated the existence of kinetic isotope effects i.e. different rates of reactions for isotopic atoms and molecules. Washburn and Urey (1932) found that partially electrolysed water was richer in deuterium content since protium was evolved at a faster rate at the cathode. This process was later used as a means of separation of hydrogen isotopes.

Bonhoeffer et al (1934) found that the rate of reaction of protium with bromine was three times faster than that of deuterium with bromine. Farkas and Farkas (1934) reported similar results with the photochemical reaction of hydrogen and deuterium with chlorine. Reviews of kinetic isotope effects have been given by Urey and Teal (1935) and Eidinoff (1953).

Studies of kinetic isotope effects have been extended to other elements for the purpose of elucidating reaction mechanisms. For example, Lindsay et al (1949) investigated the decomposition of oxalic acid and found that ^{12}C bonds rupture more readily than those of ^{13}C bonds. Kinetic isotope effects have also been reported for reactions involving oxygen, nitrogen, sulphur (see review article McMullen and Thode, 1963), selenium (Krouse and Thode, 1962), germanium (Brown and Krouse, 1964), and tellurium (Smithers and Krouse, 1968).

ISOTOPE ABUNDANCE VARIATIONS IN NATURE:

Stable isotopes of numerous elements have been found to vary in their natural abundances. Currently, the activity in this field of research is very great and it is difficult to keep abreast with new developments. Natural isotopic fractionation processes can be divided into two main categories:

(i) production of a stable isotope because of the radioactive decay of an unstable nuclide.

(ii) variations which result during mass dependent processes.

The later may be further characterized as purely physical, purely chemical, or biological (a combination of physical and chemical) processes.

Diffusion is an example of a physical process. If

the mechanism is interstitial, the isotopic diffusion coefficients are inversely proportional to the (isotopic masses)$^{\frac{1}{2}}$. This has been demonstrated in a number of cases including $^{6}L_i$ and $^{7}L_i$ diffusion in rutile (Johnson and Krouse, 1966).

The vapour pressure for lighter isotopic species is higher than for that of the heavier isotope. As a result, polar regions of the world experience precipitation in which the $H_2{}^{18}O$ content is depleted by as much as 5 percent as compared to equatorial waters (Epstein and Sharp, 1959).

The exchange of oxygen isotopes between water and carbonate ion is relatively rapid and the isotopic equilibrium exchange constant has a marked temperature dependence. On this basis, a paleotemperature scale was established (Urey et al, 1948; McCrea, 1950; Epstein et al, 1951; and Clayton, 1955).

Other isotopic exchanges are much slower. For example, the exchange of oxygen isotopes between sulphate and water is so slow that it is believed that equilibrium has not been attained in many terrestrial waters (Lloyd, 1967; Longinelli and Craig, 1967).

Micro-organisms have also been found capable of demonstrating isotopic selectivity during natural conversions. For example, Rosenfeld and Silvermann (1959) found that methane produced during bacterial fermentation of methanol

was enriched in ^{12}C by over 7 percent in comparison to the methanol at any instant during the reaction. In the next section, $^{34}S/^{32}S$ variations in nature will be considered more extensively along the lines of the above discussion.

The reader is referred to the following review articles and books if he wishes more information on natural isotope variations (Ingerson, 1953; Rankama, 1954, 1963; Thode, 1953, I.U.P.A.C., 1964; Craig et al, 1964, Stout, 1967; McMullen and Thode, 1963).

CHAPTER II

SULPHUR ISOTOPE FRACTIONATION STUDIES

Investigations of natural sulphur isotope variations have proved very informative since (1) sulphur has a wide terrestrial distribution and (2) it occurs naturally in valence states over its whole range from -2 to +6.

Initial investigations were carried out by Thode et al (1949). Numerous studies have since shown that the natural $^{34}S/32_S$ abundance ratio has an overall variation of about 10 per cent. A number of features are evident in the distribution pattern. These are now discussed in reference to Figure I which summarizes a number of sulphur isotope data. Sulphur isotope variations are expressed on a $\delta\ ^{34}S$ scale in ‰ as follows:

$$\delta\ ^{34}S = \left[\frac{(^{34}S/32_S)_{sample}}{(^{34}S/32_S)_{meteorite}} - 1\right] \times 1000$$

Meteorite troilite has been found to be markedly constant in its $^{34}S/32_S$ composition. (MacNamara and Thode, 1950; Vinogradov, 1959; Thode, et al, 1961; Shima and Thode, 1961; Jenson and Nakai, 1962; Krouse and Folinsbee, 1964; Kaplan and Hulston, 1966; Hulston and Thode, 1965, Sasaki, 1967). It has also been found in carbonaceous chondrites where sulphur occurs in the elemental form and sulphate that the $^{34}S/32_S$ composition is also close to the troilite average, (Monster et al, 1965). It has been further noted

FIGURE I

Sulphur Isotope Distribution in Nature

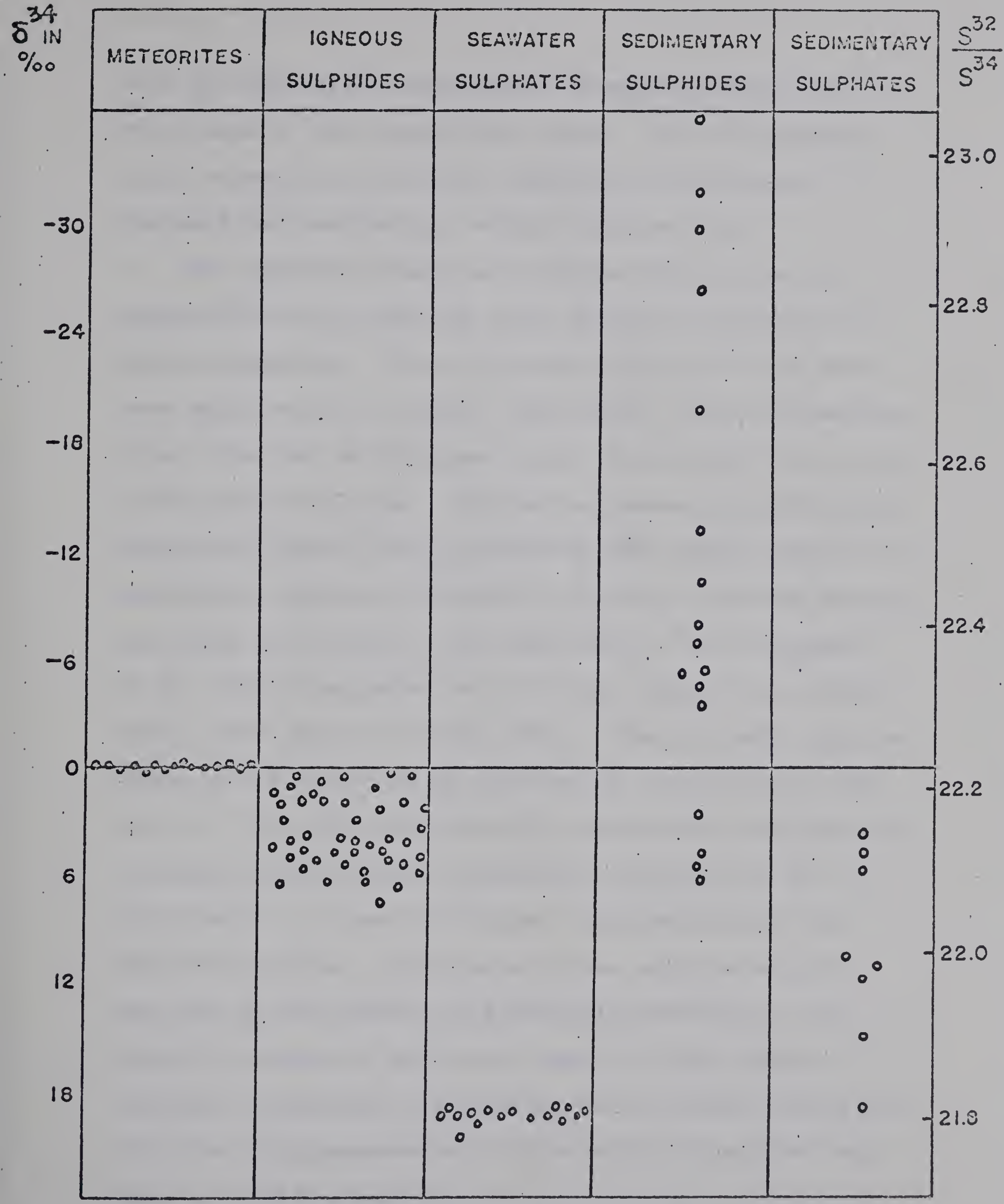


FIG. 1 SULPHUR ISOTOPE DISTRIBUTION IN NATURE

that the meteoritic composition is approximately the mean value of the terrestrial spread. For this reason, it is convenient to choose meteoritic troilite as standard for designating sulphur isotope data.

The question arises as to whether the meteoritic composition is in fact the same as the terrestrial primordial abundance. Since igneous sulphides should have less opportunity to undergo significant isotopic fractionation, then one would expect their composition to be close to the primordial one. Studies on igneous sulphides have shown that their $^{34}S/32_S$ abundances are indeed close to the meteoritic reference, although a number of igneous deposits are found to be about 1 °/₀₀ enriched in ^{34}S (MacNamara, et al, 1952; Vinogradov, et al, 1956; Kulp, et al, 1956; Sakai, 1957; Ryznar, et al, 1967). Since by mass spectrometry, it is possible to distinguish variations of less than 0.1 °/₀₀, this difference is significant experimentally. In terms of the overall terrestrial variation of 100 °/₀₀ it is small. It must be further realized that in the meteorite studies, the interior of an extraterrestrial body may be the subject of examination whereas we are unable to obtain an equivalent sample of the earth's interior. Therefore the question as to whether meteoritic troilite is representative of the worlds primordial abundance is still an open one.

The contribution of physical processes to the overall fractionation of sulphur isotopes in nature is probably small. One reason is that for physical processes to be extensive, high mobilities are generally required. In the case of terrestrial sulphur occurrences, this usually implies high temperatures. For example, as mentioned in the introduction, the vapour pressure of $H_2{}^{16}O$ is higher than $H_2{}^{18}O$ and as a result, the $^{18}O/16_O$ ratio is altered considerably in the meteorological cycle. Terrestrial conditions fortunately do not permit the analogous process with H_2S although similar isotope fractionation should be demonstrable in the laboratory. In the case of isotopic partitioning between a gas and a liquid, the isotopic composition of each phase is uniform and all atoms of the element are given the opportunity of participation (or in a closed system, all atoms of the liquid and gas phases can be in equilibrium). In order to realize the attending isotope effect in solid-liquid or solid-gas isotopic partitioning the interior atoms of the solid must be sufficiently mobile to exchange with the surface atoms. Otherwise, the phase partitioning involves only the surface atoms of the solid. In any case, with the possible exception of some organic compounds, sulphur isotopic phase partitioning generally occurs terrestrially at high temperatures e.g. in volcanic processes or magmatic sulphide deposit

formation. In any process the isotope effect will have an $e^{-\Delta E/kT}$ dependence where ΔE is the difference in isotopic energies for the process (e.g. difference in isotopic activation energies of diffusion). Therefore isotope effects generally decrease with temperature. Nevertheless, phase partitioning effects are measureable in high temperature sulphide deposits. For example in the Quemont deposit, Ryznar et al, (1967) found the overall variation of the $^{34}S/32_S$ ratio to be less than 2 δ-units. Despite this small spread, they found trends. For example, the higher melting point minerals, pyrite and pyrrhotite, were enriched in ^{34}S in comparison to the lower melting point minerals sphalerite and chalcopyrite. This was explained on the basis of liquid-solid isotopic partitioning during solidification. The solid, or more condensed phase was enriched in ^{34}S. The higher melting point minerals which formed first were therefore enriched in ^{34}S. The sphalerite and chalcopyrite which formed later at lower temperatures had to do so from the remaining melt which was depleted in ^{34}S.

It would seem that other physical processes such as diffusion also contribute little to the overall $^{34}S/32_S$ variations. Again, high temperatures would be involved for most terrestrial occurrences e.g. metallic sulphides. There may be significant isotope fractionation in

biophysical processes such as diffusion across cell membrane. This possibility has not been directly demonstrated. It is interesting however that in studies of $SO_3^=$ reduction by Salmonella sp by Krouse, et al (1967, 1968), the attending isotope effects are much higher than in the inorganic chemical reduction suggesting that isotope fractionation may be occurring in biophysical steps of the process.

It follows that the greater part of $^{34}S/32_S$ fractionation in nature results from chemical (or biophysical) processes. From considerations of statistical mechanics, the heavy ^{34}S should be favoured in the cases where sulphur occurs in the higher valence states. This results since the summation of more fundamental vibrational frequencies are involved in evaluating the isotopic partition function ratios for the multi-atomic molecules. The terrestrial distribution is consistent with theoretical predictions. Samples of seawater sulphate have been found to be markedly constant and enriched in ^{34}S by about 20 δ-units with respect to the meteoritic reference. (Trofimov, 1949; Szabo et al, 1950; Kulp et al, 1956; Thode, Monster, and Dunford, 1961). This suggests that sulphate ion is thoroughly mixed throughout the oceans of the world. Sedimentary sulphates are generally enriched in ^{34}S while sedimentary sulphides are enriched in the

lighter ^{32}S. However, a number of Pb-Zn sulphide deposits in western Canada have been found to be significantly enriched in ^{34}S (Evans, 1965; Sasaki, 1967). Reference will be made to these later.

To find an explanation of how the distribution of sulphur isotopes in nature has occurred, Tudge and Thode (1950) calculated the values of equilibrium constants for isotopic exchange reaction:

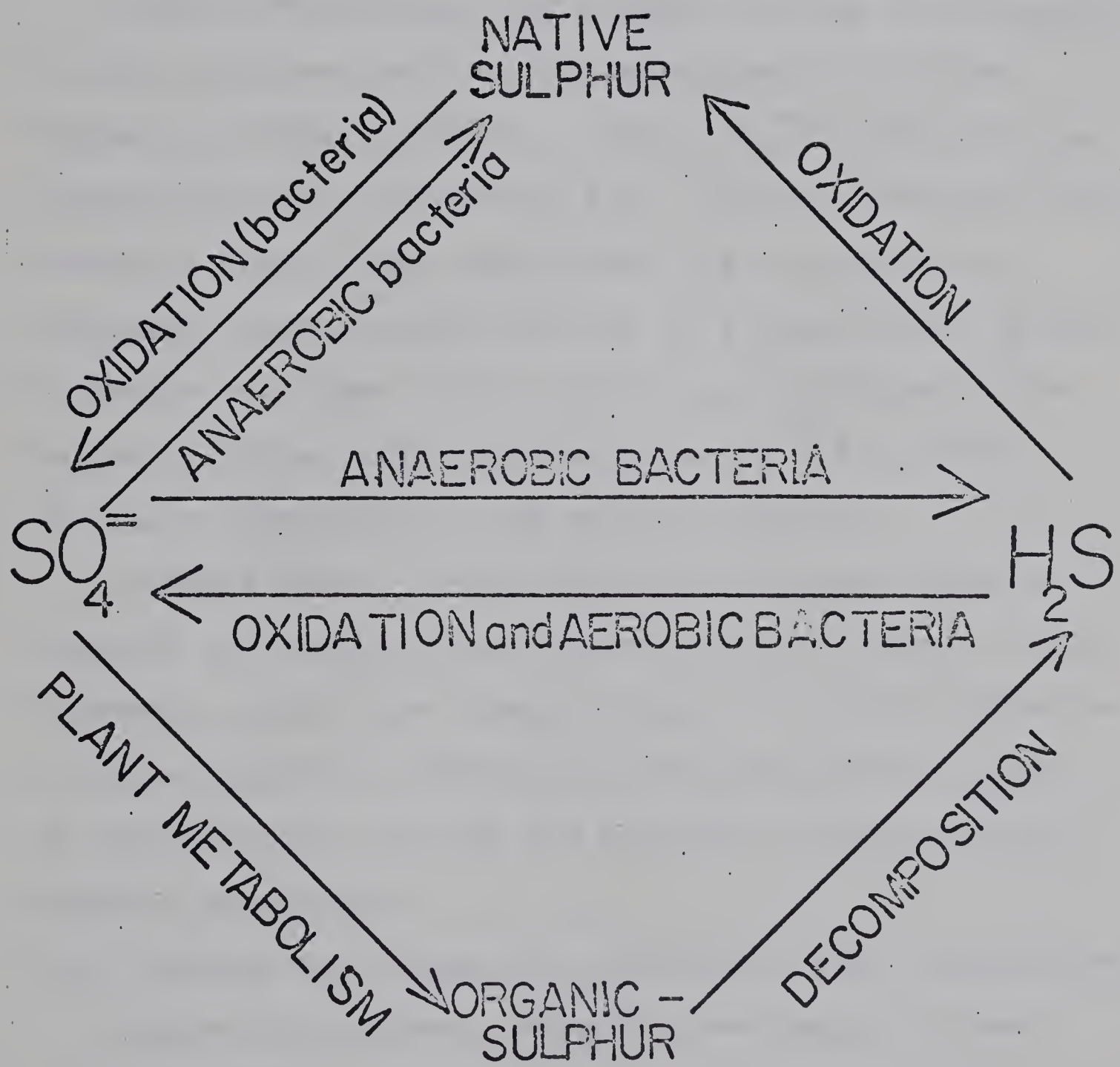
$$^{32}SO_4^{=} + H_2{}^{34}S \overset{K}{\rightleftharpoons} {}^{34}SO_4^{=} + H_2{}^{32}S$$

At 25°C, the theoretical equilibrium constant for this exchange was found to be 1.072 indicating that there should be 7.2% more ^{34}S in sulphate than in hydrogen sulphide at the establishment of equilibrium. It is interesting to note that the overall spread in the terrestrial $^{34}S/32_S$ ratio is of the same order as the equilibrium constant for this exchange reaction which involves the highest and lowest valence state of sulphur occurrence in nature. It has been shown that the exchange between $SO_4^{=}$ and H_2S does not occur readily under normal conditions (Voge and Libby, 1937; also this study). Therefore Szabo et al (1950) suggested that perhaps the well known biological sulphur cycle in nature (Figure II) might be a plausible means of effecting fractionation of sulphur isotopes in the above exchange. In this cycle, sulphate is being

FIGURE II

Sulphur Cycle in Nature

(after Szabo et al, 1950)


NATIVE SULPHUR
OXIDATION (bacteria)
ANAEROBIC bacteria
OXIDATION
ANAEROBIC BACTERIA
$SO_4^=$
H_2S
OXIDATION and AEROBIC BACTERIA
PLANT METABOLISM
ORGANIC - SULPHUR
DECOMPOSITION

continuously reduced either by bacterial reduction under anaerobic conditions or through plant metabolism, while the sulphides and H_2S are being oxidized to sulphur and sulphate.

Direct verification for sulphur isotope fractionation in this cycle was made in the investigations of the Cyrenaican lakes in Africa. There, $SO_4^=$ in solution was microbiologically reduced to H_2S. Oxidizing bacteria also abound in these lakes and oxidize H_2S in solution to elemental sulphur, which settles as a layer on the bottom. MacNamara and Thode (1951) found the S^0 produced at the bottom of these lakes to be depleted in ^{34}S by about 32 °/₀₀ in comparison to the soluble sulphate.

Other evidence of the biological sulphur cycle was found in the sulphur wells of Louisiana and Texas, U.S.A. Elemental sulphur was found to occur in calcium carbonate in these deposits. Reduction of the surrounding gypsum to form hydrogen sulphide and elemental sulphur had two possible mechanisms:

(a) Sulphate was organically reduced at high temperatures since oil is found around the periphery of these salt domes.

(b) Sulphate was reduced by bacteria. In this case the petroleum present would supply the source of energy for the bacteria.

To establish the exact mechanism of the process, Thode, et al (1954) investigated the $^{34}S/32_S$ content of the gypsum and the sulphur and sulphide and found that the ^{34}S content of the sulphate was about 40‰ higher than that of elemental sulphur and 50‰ higher than the sulphides. The first high temperature process is incapable of producing such large isotopic fractionations, whereas the second low temperature process of bacterial reduction can certainly do so.

Microbiological sulphur isotope fractionation in the laboratory was subsequently demonstrated by Thode et al (1951). They reported a 1% depletion of ^{34}S in hydrogen sulphide produced during the reduction of sulphate by Desulphovibrio desulphuricans. A large temperature coefficient for such isotope fractionation was reported by Jones et al (1956) who found that the fractionation could be increased to 25 ‰ by using a higher sulphate concentration and reducing the temperature to the range 14°C to 20°C. Hence the isotope enrichment can be controlled by the temperature regulation of the rate of reduction. Harrison and Thode (1958) investigated sulphate reduction by Desulphovibrio desulphuricans in more detail. They proposed a two-step mechanism for the

reduction in which the first step involved little or no isotope effect while the following step involved S - O bond rupture. In the latter step, the ^{32}S - O breaks 1.022 times as fast as ^{34}S - O (Harrison and Thode, 1957). If the first step were rate controlling, the isotope effect would be negligible whereas if the step involving bond rupture controlled the rate, the maximum isotope fractionation would be observed. Intermediate isotope fractionation result when the two steps occur at comparable rates.

Kaplan and Rittenberg (1962, 1964) have extended the studies of isotope fractionation in the natural sulphur cycle. Figure IIa summarizes these studies. The isotope enrichment of the final and intermediate products are designated by 32 and 34 for ^{32}S and ^{34}S enrichment respectively, while N signifies negligible fractionation.

In nature, it is sometimes found that co-existing sulphide and sulphate may have an isotopic difference which is much larger than the 22‰ resulting during sulphate reduction. In some cases these larger fractionations may be the result of extensive conversion of sulphate as discussed by Nakai and Jensen (1964). This is illustrated in Figure III.

FIGURE II-a

Isotope Fractionation in Natural Sulphur Cycle

(after Kaplan and Rittenberg, 1962 and 1964)

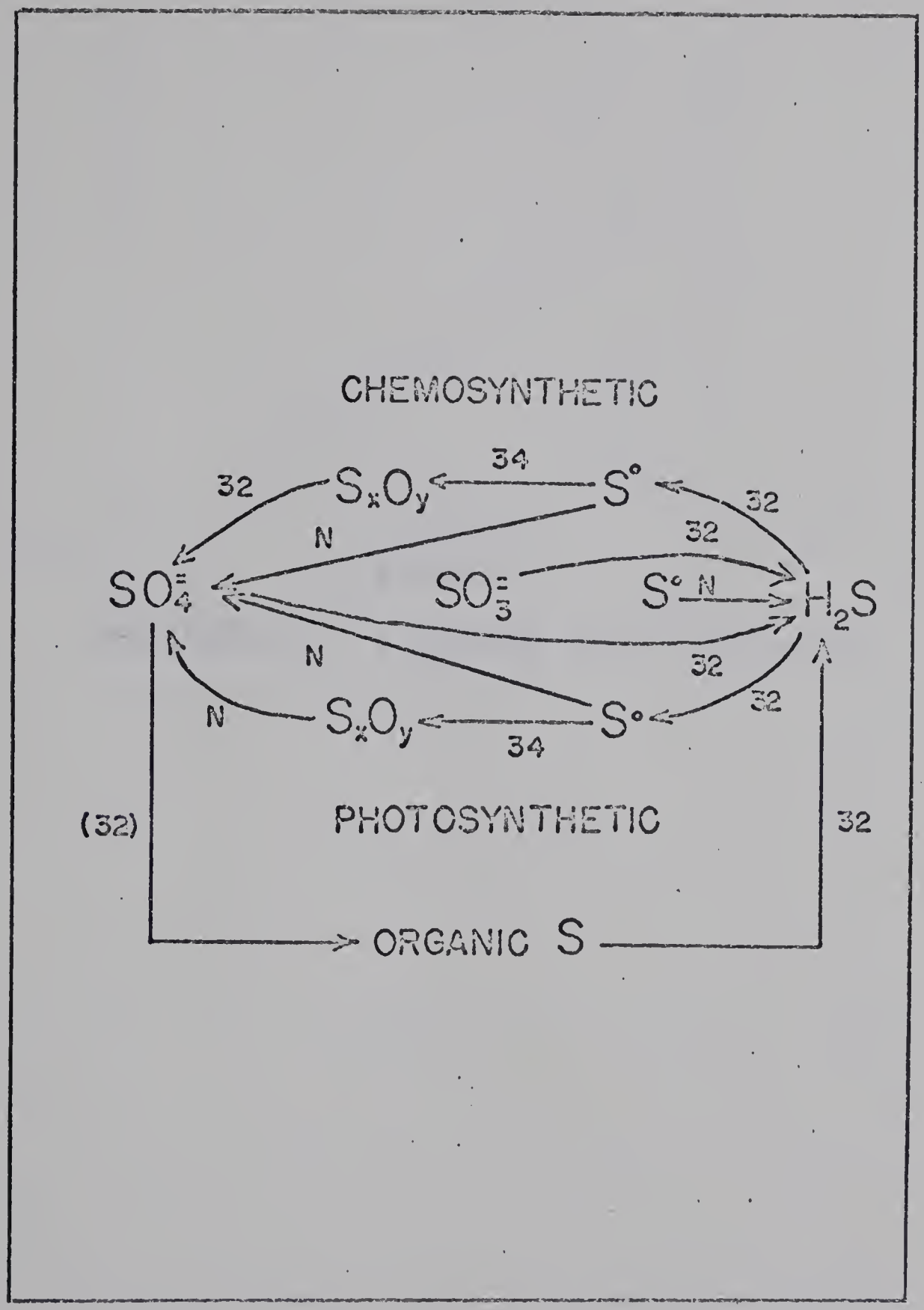
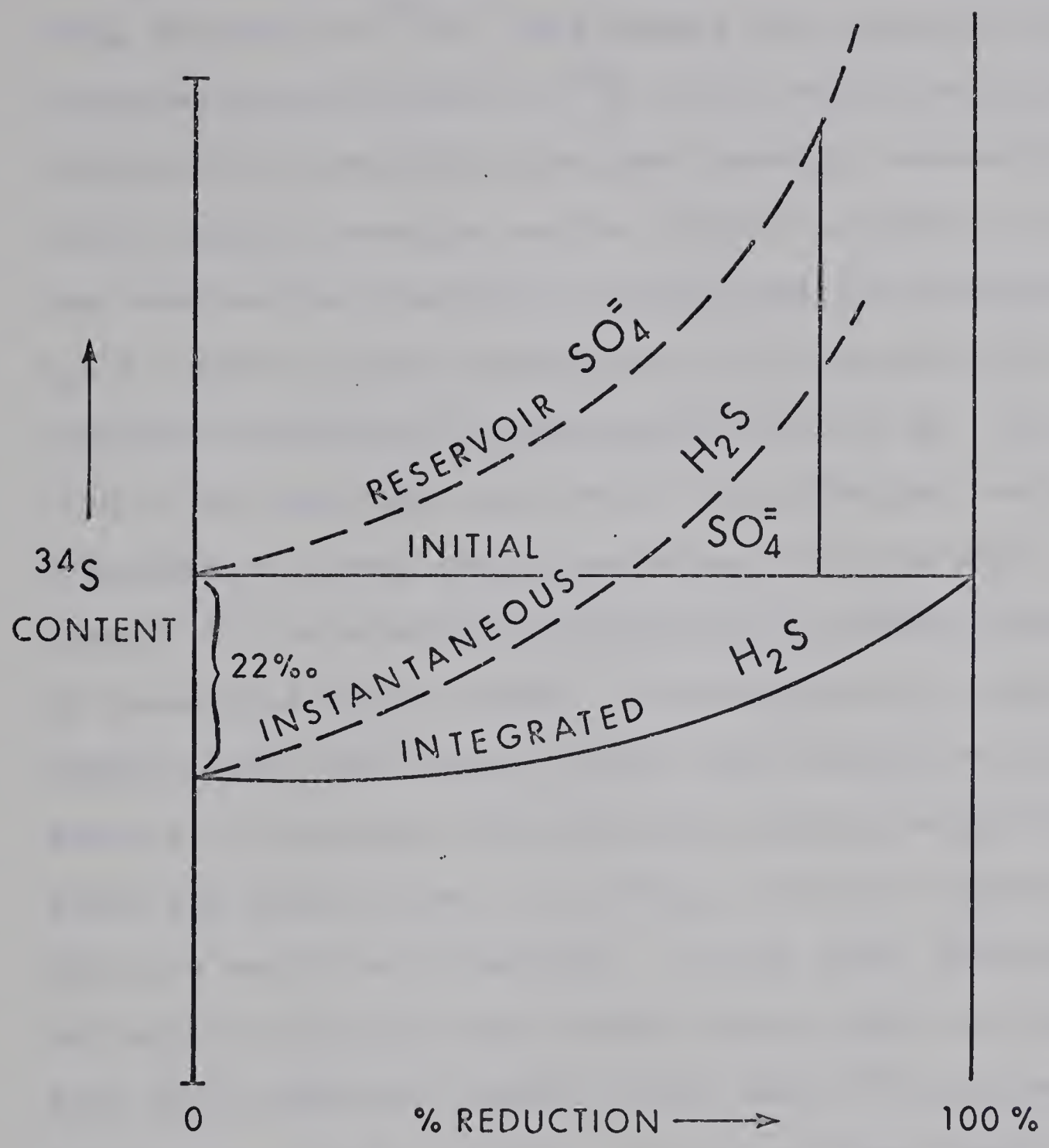

CHEMOSYNTHETIC
34
32
S_xO_y
S°
32
N
32
$SO_4^=$
$SO_3^=$
S° N
H_2S
N
32
N
S_xO_y
S°
32
34
(32)
PHOTOSYNTHETIC
32
ORGANIC S

FIGURE III

Variation of ^{34}S Content with % Reduction


RESERVOIR $SO_4^=$
H_2S
INITIAL
$SO_4^=$
^{34}S
CONTENT
22‰
INSTANTANEOUS
H_2S
INTEGRATED
0
% REDUCTION ——→
100 %

The H_2S which is produced at any instant is typically 22‰ depleted in ^{34}S. This causes the unreacted $SO_4^=$ to become more enriched in ^{34}S as the reduction proceeds. The integrated H_2S must have the same isotopic composition at 100 percent reaction as the initial sulphate. If one examines the reservoir sulphate and the integrated H_2S at say 80 percent reduction, it is seen that the isotopic difference is much greater than 22‰. In nature, one can find cases where the reduction has only proceeded to a very small percentage of conversion. One example is the studies on hotsprings of Western Canada by Sasaki and Krouse (1966). The sulphates of these waters range from +10 to +24‰ with respect to the meteoritic reference while the microbiologically produced H_2S ranges from -5 to +5‰. In these studies, H_2S is a very minor component. On the other hand, Pb and Zn sulphide deposits near Banff (Evans, 1965) and the Pine Point deposits (Sasaki, 1966) have ^{34}S enrichment ranging from +10 to +30‰. In all of these cases, it would appear that the source of sulphur was ancient sea water sulphate. In the case of the Pb - Zn deposits, the conversion must have been almost complete in order that the isotopic composition of the sulphide retain the characteristics of the original sulphate.

There are however some occurrences where co-existing sulphate and sulphide show a variation of larger than 22‰ and there is no evidence of a reservoir effect. Further, instantaneous isotope fractionations of larger than 1.022 have been found in laboratory experiments. Kaplan and Rittenberg (1964) found that during $SO_4^=$ reduction by Desulphovibrio desulphuricans and $SO_3^=$ reduction by Saccaromyces cerevisiae, that the lighter ^{32}S-containing species could be reduced faster than the heavier species by a factor of as high as 1.04. Krouse et al (1968) in an extensive study found similarly high isotopic fractionation during $SO_3^=$ reduction by Salmonella. A satisfactory explanation of why micro-organisms can exhibit much higher isotopic selectivity than equivalent inorganic processes, has not been offered. There are many possibilities. Krouse et al (1968) suggested that two consecutive isotopic fractionating steps with an intervening reservior could account for their data. There are also the possibilities of a partial equilibrium isotope exchange effect occurring at some step in the process or that biophysical processes such as diffusion contribute to the isotope fractionation.

It is therefore seen, that while the sulphur isotope exchange involving H_2S and $SO_4^=$ has theoretical implications, it has not been identified directly in nature.

It is conceivable that this equilibrium might be approached in a biological redox system, but most observations to date have been interpreted solely in terms of kinetic effects in steps within the biological sulphur cycle.

Other exchange reactions have been suggested to account for sulphur isotope fractionation in specific natural settings. Vinogradov (1958) suggested the following possibilities.

$$3\ {}^{32,34}S_2 + 4\ H_2O \rightleftharpoons 4\ H_2\ {}^{32}S + 2\ {}^{34}SO_2$$

$$4\ H_2\ {}^{32,34}S + O_2 \rightleftharpoons 2\ H_2O + 2\ H_2\ {}^{32}S + 2\ {}^{34}S$$

Sakai (1957) measured ${}^{34}S/32_S$ ratios in SO_2 and H_2S* from Japanese fumaroles. Their results appeared to be consistent with the exchange

$$H_2S + 2\ H_2O \rightleftharpoons SO_2 + 3\ H_2$$

---

* It is interesting to note that in volcanic studies of New Zealand, where all of the sulphur compounds were studied, Rafter (1958) found that the mean ${}^{34}S/32_S$ content was close to the meteoritic reference.

In conclusion it appears that sulphur isotopic exchange is encountered in geological settings and perhaps in biological systems.

Although a number of exchanges in the laboratory have been studied using ^{35}S, very few results have been obtained using stable sulphur isotopes. Both the radiosulphur and stable sulphur isotope exchange studies to date are summarized in Chapter IV. This thesis describes a number of sulphur isotope exchanges which have been monitored in our laboratory by determining alterations to the $^{34}S/32_S$ abundance ratio using the mass spectrometer.

CHAPTER III

THEORY

EQUILIBRIUM ISOTOPE EFFECT:

Marked differences in the equilibrium constants of isotopic exchange reactions were first reported by Rittenberg and Urey (1933,1934). Statistical mechanical considerations were applied by Urey and Grieff (1935), to the calculation of theoretical equilibrium exchange constants in terms of "distribution functions' and summation over states" terms. Further simplification was developed by Urey (1947) and Bigleisen and Mayer (1947). This made it possible to calculate the equilibrium constants of isotopic reactions with merely the knowledge of vibrational frequencies of the isotopic molecules.

A typical isotope-exchange reaction may be written as:

$$a\ A_1 + b\ B_2 \rightleftharpoons a\ A_2 + b\ B_1 \qquad [1]$$

A and B are molecules containing the element of interest. The subscripts 1 and 2 refer to the light and heavy isotope respectively of the element. From thermodynamical considerations, the change in standard free energy for the above reaction is related to the equilibrium exchange constant as follows:

$$-RT \ln K = \Delta F^\circ \qquad [2]$$

where,

$$\Delta F^0 = a F_{A_2} + b F_{B_1} - a F_{A_1} - b F_{B_2} = -RT \ln K \qquad [3]$$

From statistical mechanics,

$$F = E_0 + RT \ln N - RT \ln Q \qquad [4]$$

where,

F = Gibb's free energy

E_0 = zero point energy

N = Avagadro's number

and Q = the partition function

The partition function 'Q' is a summation over all energy states defined as:

$$Q = \sum_n g_n e^{-\varepsilon_n/kT} \qquad [5]$$

where,

g_n = the statistical weight factor of the energy state ε_n.

In case of only one molecule in a unit volume instead of one mole, the number N is taken as unity and hence the second term on the right hand side of equation [4] vanishes. Substituting [4] in [3] and simplifying gives the following expression for the equilibrium constant:

$$K = \left(Q_{A_2}/Q_{A_1}\right)^a \left(Q_{B_1}/Q_{B_2}\right)^b \exp - \left\{ \frac{a\,E_{0A_2} + b\,E_{0B_1} - a\,E_{0A_1} - b\,E_{0B_2}}{kT} \right\} \qquad [6]$$

where the energy values are measured with respect to a suitable reference state. If instead of the zero point energy we refer all energies to the minimum of the potential energy curves, equation [6] reduces to the simple form:

$$K = \left(Q_{A_2}/Q_{A_1}\right)^a \left(Q_{B_1}/Q_{B_2}\right)^b \qquad [7]$$

The equilibrium constant is simply the product of the total isotopic partition-function ratios for the two molecules undergoing exchange.

It will be shown that only the vibrational partition function need be considered. The translational partition function is the same as the classical one for all temperatures and the rotational partition function is classical at room temperature with the exception of hydrogen. As a result, in taking isotopic partition function ratios, rotational and translational contributions cancel.

Considering a volume V and following Herzberg (1956) we have for diatomic or linear polyatomic molecules:

$$Q = \frac{(2\pi MkT)^{3/2}}{h^3} \times \frac{VkT}{hcB} \prod_i^{3n-5} \frac{e^{-Ui/2}}{(1-e^{-Ui})} \left[\frac{1}{\sigma} \prod (2I+1) \prod \frac{(2I+1)^2}{2} \right] \qquad [8]$$

and for the polyatomic molecules:

$$Q = \frac{(2\pi MkT)^{3/2}}{h^3} \times V \times \left[\frac{\pi}{ABC}\left(\frac{kT}{hc}\right)^3\right]^{\frac{1}{2}} \prod_{i}^{3n-6} \frac{e^{-Ui/2}}{(1-e^{-Ui})} \left[\frac{1}{\sigma}\prod(2I+1)\prod\frac{(2I+1)^2}{2}\right] \quad [9]$$

where,

n = the number of atoms in the molecule

M = total molecular mass

k = Boltzman constant

A, B, C are the rotational constants of the molecules, related to its principal moments of inertia by the relation:

$$A = {}^{h}/_{8\pi^2 cI_A}$$

The term U_i occurring in the exponential is related to the $i^{\underline{th}}$ fundamental frequency ν_i of the molecule and is given by:

$$U_i = {}^{\varepsilon}i/kT = {}^{h\nu}i/kT$$

The product $\prod_i$ extends over all i fundamental frequencies of the polyatomic molecule and the symmetry factor σ accounts for the identity of the nuclei. The bracketed terms in I are the nuclear spin factors which cancel out at a later stage and have no bearing on the determination of the isotope effect. The following fundamental assumptions are implied in the development of the above expressions:

(1) The rigid rotator model is generally adopted for

the rotational part of Q, and it is assumed that in all cases this term will have reached its classical or high temperature limit. The details of these assumptions have been discussed by Herzberg (1956). Further, it is supposed that no vibration-rotation interactions are involved.

(2) The harmonic oscillator model is adopted for the vibrational partition function. Although the vibrations of real molecules are not harmonic in nature, the assumption is not too bad when ratios of partition functions for isotopic molecules are considered, provided the observed fundamental frequencies are used, and the temperature is low enough to allow for appreciable populations of only the lower vibrational states. However, anharmonicity corrections are significant at higher temperatures. In very few cases the anharmonicity constants have been studied and for majority of molecules only the observed fundamental frequencies are available.

(3) Because of the identical nature of the potential energy curves for isotopic molecules only the evaluation of the energies of molecular vibrations is required. For a given molecule the vibrational energies may be measured with respect to the bottom of the potential energy curve, since the correction

term related to this energy to the arbitrary common zero for all molecules considered would appear both in the numerator as well as the denominator of the expression for equilibrium constant.

Thus for simplicity (omitting the symmetry factors and the nuclear spin) we have for two isotopic polyatomic molecules:

$$Q_{2/Q_1} = \left(M_{2/M_1}\right)^{3/2}\left(\frac{I_{A_2} I_{B_2} I_{C_2}}{I_{A_1} I_{B_1} I_{C_1}}\right)^{\frac{1}{2}} \prod_{i}^{3n-6} \frac{\bar{e}^{U_{2i}/2}}{(1-\bar{e}^{U_{2i}})} \times \frac{(1-\bar{e}^{U_{1i}})}{\bar{e}^{U_{1i}/2}} \qquad [10]$$

It has been shown through different approaches by Urey (1947) and Bigeleisen and Mayer (1947) that this expression can be evaluated without the considerations of moments of inertia. Both sides of equations [8] and [9] are multiplied by $\left[M_{1/M_2}\right]^{3/2n}$ where 'n' is the number of isotopic atoms exchanged and M_1 and M_2 are the atomic weights of the isotopic atoms. Then the right hand sides of equations [8] and [9] are multiplied and divided by U_{1/U_2} and $\prod_i (U_{ii/U_{ii}})$. Then use is made of the Teller-Redlich rule (Redlich, 1935, Angus et al, 1936) according to which the quantity:

$$\prod_{i}^{3n-6} U_i^2 \prod_j M_j^3 / M^3 I_A I_B I_C$$

where M_j's are the atomic masses in the molecule, is invariant under isotopic substitution i.e. for two isotopic species:

$$\left(M_2/M_1\right)^{3/2}\left[I_{A_2}I_{B_2}I_{C_2}/I_{A_1}I_{B_1}I_{C_1}\right]^{\frac{1}{2}} = \prod_i^{3n-6} U_{2i}/U_{1i} \prod_j M_{2j}/M_{1j}^{3/2}$$

we then obtain:

$$Q_2/Q_1 = \left(M_{2j}/M_{1j}\right)^{3/2} \times U_2/U_1 \times \frac{e^{-U_2/2}(1-e^{-U_1})}{e^{-U_1/2}(1-e^{-U_2})}$$

and,

$$Q_2/Q_1 = \prod_j^{3n-6}\left(M_{2j}/M_{1j}\right)^{3/2} \prod_i^{3n-6} U_{2i}/U_{1i} \times e^{-U_{2i}/2}/e^{-U_{1i}/2} \times \frac{(1-e^{-U_{1i}})}{(1-e^{-U_{2i}})}$$

for diatomic and polyatomic molecules respectively. Since, the factors $(M_{2j}/M_{ij})^{3/2n}$ appear in both the numerator and denominator, it will not affect the equilibrium constant and hence the equilibrium constant can be expressed as:

$$K = \left(Q'_{2A}/Q'_{1A}\right)^a / \left(Q_{2B}/Q'_{1B}\right)^b$$

where; $Q'_2/Q'_1 = \left(M_1/M_2\right)^{3/2n} \times Q_2/Q_1$ is the modified ratio.

Thus the equilibrium constant can be calculated by knowing only the vibrational frequencies of the isotopic molecules. These frequencies are usually calculated using spectroscopic force equations and observations on a more abundant isotope. Sometimes the isotopic frequencies can be obtained by direct observation. The above expression

excludes the anharmonicity in the vibrational energy, and assumes that the rotational partition functions have reached classical values. The ratio of symmetry numbers which have been omitted for simplicity in the theoretical treatment will be unity if the molecules under consideration consists of only one atom of the element for which an exchange is considered or if the molecule contains more than one such atom but these atoms are spatially indistinguishable in the molecule and are all exchanged in the reaction.

Hence, for diatomic molecules:

$$Q_{2/Q_1} = {}^{U_{2/U_1}} \times \frac{e^{-U_{2/2}}(1-e^{-U_1})}{e^{-U_{1/2}}(1-e^{-U_2})}$$

and for polyatomic molecules:

$$Q'_{2/Q_1}{}' = \prod_i^{3n-6} U_{2i/U_{1i}} \times \frac{e^{-U_{2i}}(1-e^{-U_{1i}})}{e^{-U_{1i}}(1-e^{-U_{2i}})}$$

For the evaluation of these partition function ratios, two simplifications have been developed Urey (1947) and (Bigeleisen and Mayer, 1947). The expression of Urey is;

$$\ln\left(Q'_{2/Q_1}{}'\right) = \sum_i^{3n-6} \ln\left(U_{2i/U_{1i}}\right) + \sum_i^{3n-6} \delta_i \operatorname{Coth} \chi_i$$

where, $$\chi_i = (U_{1i} + U_{2i})/4$$

and $$\delta_i = (U_{1i} - U_{2i})/2$$

The Bigeleisen and Mayer expression is:

$$Q_2'/Q_1' = 1 + \sum_i^{3n-6} G(U_i)\Delta U_i$$

where $$G(U_i) = \frac{1}{2} - \frac{1}{U_{2i}} + \frac{1}{(e^{U_{2i}}-1)}$$

and $$\Delta U_i = U_{1i} - U_{2i}$$

These functions are approximations to the exact expression for calculation purposes. The function $G(U)\Delta U$ has been tabulated for a range of values of U (Bigeleisen and Mayer, 1947).

ESTABLISHMENT OF ISOTOPIC EXCHANGE EQUILIBRIUM

In isotope exchange reactions, the rate at which atoms are exchanged depends on a number of factors such as temperature, mobility of species, mechanism of exchange etc. The assumption is made that the rate of exchange is directly proportional to the distance that the system is from isotopic equilibrium. Thus, the amount of exchange observed after a time "t" for a system initially 20‰ from equilibrium would be twenty times as great as that for a system whose original

fractionation was 1‰ from equilibrium. The attainment of isotopic exchange equilibrium is now considered using the derivation by Northrop and Clayton (1966).

Consider the exchange reaction

$$A_1 + B_2 \underset{R}{\overset{KR}{\rightleftharpoons}} A_2 + B_1 \qquad [1]$$

where A and B are molecules containing the element of interest 'X' with light and heavy isotopes 1 and 2 respectively. It is assumed that there is only one exchangeable isotope per molecule as is the case for all the systems reported in this thesis. R is the rate for the reverse reaction in (moles/second) and it will generally be a function of several variables such as temperature, pressure, mobility etc. The rate of the forward reaction is KR (moles/second) so that the ratio of the rates is the equilibrium constant K. The equilibrium constant K is given by

$$K = [{}^2X/{}^1X]_A/[{}^2X/{}^1X]_B \qquad [2]$$

Assume that at sometime, the system contains "a" moles of A with the ratio of heavy to light isotope abundance $\left[\frac{{}^2X}{{}^1X}\right]_A = x$ and "b" moles of B with $\left[\frac{{}^2X}{{}^1X}\right]_B = y$. On the condition that x and y << 1, then A contains ax moles of ${}^2X$ and B contains bx moles of ${}^2X$. At this point, it is noted that x and y for ${}^{34}S/{}^{32}S$ are about 0.04. For other elements such as O, N, C and H, the above

approximation is more valid since ^{18}O, ^{15}N, ^{12}C, and ^{2}H are of lower abundance. The conditions that x and y << 1 considerably simplify the expressions derived below. Further, the derived expression equates parameters to relative isotope ratios as measured by the mass spectrometer. In more exact derivations, absolute abundance measurements would be necessary to utilize the equations.

The total number of moles of ^{2}X for the system is constant. i.e.

$$T = ax + by \qquad [3]$$

Consider now the increase of ^{2}X in phase A with time

$$\frac{dx}{dt} = \frac{1}{a} (RKy - Rx) \qquad [4]$$

Define $\alpha = \frac{x}{y}$ at any time t

$$\frac{dx}{dt} = \frac{Rx}{a} (\frac{K}{\alpha} - 1) \qquad [5]$$

Differentiating [3] and substituting from [5];

$$-\frac{dy}{dt} = \frac{a}{b} \frac{dx}{dt} = \frac{Rx}{b} (\frac{K}{\alpha} - 1) \qquad [6]$$

Substituting [5] and [6] into

$$\frac{d\alpha}{dt} = \frac{d\left[\frac{x}{y}\right]}{dt} = \frac{y \frac{dx}{dt} - x \frac{dy}{dt}}{y^2} \qquad [7]$$

gives

$$\frac{d\alpha}{dt} = R\ \left(\frac{a\alpha + b}{ab}\right)\ (K - \alpha) \qquad [8]$$

If α is approximated by unity so that $(a\alpha + b) \approx (a + b)$, then integration between the limits $t = 0$ to $t = t_{final}$ and $\alpha = \alpha_{initial}$ to $\alpha = \alpha_{final}$ yields

$$-\ln \frac{K - \alpha_f}{K - \alpha_i} = \frac{a + b}{ab} \int_o^{t_f} R(t)dt = F(t_f) \qquad [9]$$

$F(t)$ is not a function of isotopic composition.

Northrop and Clayton carried out a series of experiments where the initial α_i was varied, and the reactions carried out for a fixed time so that the right hand side of [9] was constant. In the experiments of this thesis, α was periodically determined throughout any one experiment. Therefore expression 9 was used in terms of selected time intervals Δt in any one experiment where α_i was the value of α at the beginning of Δt and α_f, the value at the end of the interval.

Therefore, for constant Δt values, the ratio $\frac{K - \alpha_f}{K - \alpha_i}$ is constant which implies that $\frac{\alpha_f - \alpha_i}{K - \alpha_i}$ is also constant. Since the α's and K are nearly unity, $\ln \alpha \approx 1 + \alpha$ so that

$$\frac{\ln \alpha_f - \ln \alpha_i}{\ln K - \ln \alpha_i} = -\frac{1}{\beta} \qquad [10]$$

and $\ln \alpha_i = \ln K + \beta (\ln \alpha_f - \ln \alpha_i)$. Therefore, a plot of $(\ln \alpha_f - \ln \alpha_i)$ against $\ln \alpha_i$ will yield a straight line of slope B and intercept ln K. If equilibrium is attained for a selected time interval, then

$$\ln \alpha_f = \ln K \text{ and } \beta = -1.$$

For samples not in equilibrium, the slope B ranges from -1 down to $-\infty$.

THEORETICAL CALCULATIONS:

Tudge and Thode (1950) and Sakai (1958) have carried out theoretical calculations of equilibrium constants for hypothetical sulphur isotope exchange reactions. Table I is reproduced from Tudge and Thode (1950). The tabulation follows the system of Urey (1947). Values of K are in the body of the table at the intersection of the row and column corresponding to the participating molecules. $K >> 1$ means that ^{34}S is favoured in the molecule listed in the left hand column.

TABLE I

EQUILIBRIUM CONSTANTS FOR SULPHUR EXCHANGES

(after Tudge and Thode, 1950)

	$\frac{S^{34}O_4^{=}}{S^{32}O_4^{=}}$	$\frac{S^{34}O_3}{S^{32}O_3}$	$\frac{S^{34}O_2}{S^{32}O_2}$	$\frac{S^{34}CO}{S^{32}CO}$	$\left[\frac{CS_2^{34}}{CS_2^{32}}\right]^{\frac{1}{2}}$	$\left[\frac{S_3^{34}}{S_3^{32}}\right]^{\frac{1}{3}}$	$\frac{S^{34}CN^-}{S^{32}CN^-}$	$\left[\frac{S_2^{34}}{S_2^{32}}\right]^{\frac{1}{2}}$	$\frac{H_2S^{34}}{H_2S^{32}}$	$\frac{PbS^{34}}{PbS^{32}}$	$\frac{S^{34}=}{S^{32}=}$	°C.
$\frac{Q_2'}{Q_1'}$	1.101	1.096	1.053	1.022	1.021	1.018	1.016	1.015	1.015	1.010	1.000	0
	1.088	1.084	1.045	1.019	1.019	1.016	1.014	1.013	1.013	1.009	1.000	25
$\frac{S^{34}O_4^{=}}{S^{32}O_4^{=}}$	1.000	1.005	1.046	1.077	1.078	1.082	1.084	1.085	1.085	1.090	1.101	0
		1.004	1.041	1.068	1.068	1.071	1.073	1.074	1.074	1.078	1.088	25
$\frac{S^{34}O_3}{S^{32}O_3}$		1.000	1.041	1.072	1.073	1.077	1.079	1.080	1.080	1.085	1.096	0
			1.037	1.064	1.064	1.067	1.069	1.070	1.070	1.074	1.084	25
$\frac{S^{34}O_2}{S^{32}O_2}$			1.000	1.030	1.031	1.034	1.036	1.037	1.037	1.043	1.053	0
				1.026	1.026	1.029	1.031	1.032	1.032	1.036	1.045	25
$\frac{S^{34}CO}{S^{32}CO}$				1.000	1.001	1.003	1.006	1.007	1.007	1.012	1.022	0
					1.000	1.003	1.005	1.006	1.006	1.010	1.019	25
$\left[\frac{CS_2^{34}}{CS_2^{32}}\right]^{\frac{1}{2}}$					1.000	1.003	1.005	1.006	1.006	1.011	1.021	0
						1.003	1.005	1.006	1.006	1.010	1.019	25
$\left[\frac{S_8^{34}}{S_8^{32}}\right]^{\frac{1}{8}}$						1.000	1.002	1.003	1.003	1.008	1.018	0
							1.002	1.003	1.003	1.007	1.016	25
$\frac{S^{34}CN^-}{S^{32}CN^-}$							1.000	1.001	1.001	1.006	1.016	0
								1.001	1.001	1.005	1.014	25
$\left[\frac{S_2^{34}}{S_2^{32}}\right]^{\frac{1}{2}}$								1.000	1.000	1.005	1.015	0
									1.000	1.004	1.013	25
$\frac{H_2S^{34}}{H_2S^{32}}$									1.000	1.005	1.015	0
										1.004	1.013	25
$\frac{PbS^{34}}{PbS^{32}}$										1.000	1.010	0
											1.009	25
$\frac{S^{34}=}{S^{32}=}$											1.000	0
												25



CHAPTER IV

STUDIES OF SULPHUR ISOTOPE EXCHANGE

STUDIES WITH RADIOSULPHUR:

Radioactive isotopes are used extensively as tracers in chemical reactions. Labelled compounds of many common elements are now available for use in most laboratories. Radiosulphur ($_{16}S^{35}$) has been used as a suitable tracer for a number of sulphur isotope exchange reactions.

Anderson (1936) produced radiosulphur for the first time by neutron bombardment of carbon tetrachloride:

$$_{17}Cl^{35} + _{0}n^{1} \rightarrow {}_{16}S^{35} + {}_{1}H^{1}$$

Another method used for the production of radiosulphur is deuteron bombardment of sulphur:

$$_{16}S^{34} + {}_{1}D^{2} \rightarrow {}_{16}S^{35} + {}_{1}H^{1}$$

In both of these methods, radiophosphorous of half life 14.5 days is formed as an impurity, but this is readily removed.

Radiosulphur (^{35}S) decays by β^- emission with a half life of 87.1 days. The maximum energy of these particles is about 0.17 Mev and therefore, the penetrating power is low (i.e. 0.015 g/cm.). As a result, precise determinations of the activities and therefore quantitative measurements are difficult.

Table II is an extension of that of Wahl and Bonner (1951)

and summarizes a number of exchange reactions which have been investigated with radiosulphur (S^*).

STUDIES WITH STABLE ISOTOPES OF SULPHUR:

Using the well known methods of statistical mechanics, Tudge and Thode (1950) have calculated partition function ratios for many isotopic sulphur compounds. These partition function ratios were utilized to determine equilibrium constants for many hypothetical exchange reactions involving ^{32}S and ^{34}S as shown in Table I. It is seen that significant sulphur isotope fractionation is predicted. In a number of exchanges, equilibrium constants have been measured experimentally to check the theoretical predictions.

The isotope exchange between H_2S and $S^=$ in solution has been investigated and the equilibrium constant for reaction

$$H_2{}^{32}S\ (g) + H\ {}^{34}S^-\ (sol'n) \rightleftharpoons H_2{}^{34}S\ (g) + H\ {}^{32}S^-\ (sol'n) \quad [a]$$

found to be 1.006 at 25°C (Szabo, reported in Tudge and Thode, 1950). The theoretical equilibrium constant for the reaction

$$H_2{}^{32}S\ (g) + {}^{34}S^=(sol'n) \rightleftharpoons H_2{}^{34}S\ (g) + {}^{32}S = (sol'n) \quad [b]$$

is 1.013 at 25°C (Tudge and Thode, 1950). It is expected

that the (K - 1) for reaction [a] should be about $\frac{1}{2}$ of (K - 1) of reaction [b] and thus the experimental determination seems to agree well with the theoretical prediction.

The theoretical equilibrium constant for the reaction:

$$H_2\,{}^{34}S + \tfrac{1}{2}\,C\,{}^{32}S_2 \rightleftharpoons H_2\,{}^{32}S + \tfrac{1}{2}\,C\,{}^{34}S_2$$

was found to be 1.006 at 25°C, (Tudge and Thode, 1950).

Douglas et al (1949) reported that CS_2 and H_2S did not exchange in benzene solution but it was felt that an exchange might take place in carbon disulphide solution through the reaction:

$$H_2S + CS_2 = H_2CS_3$$

Edwards and Nesbett (1948) reported that sulphur isotopes exchange $S^{=}$ (sol'n) and CS_2 through an intermediate $CS_3^{=}$. The theoretical equilibrium constant for the exchange:

$${}^{34}S^{=} + \tfrac{1}{2}\,C\,{}^{32}S_2 \rightleftharpoons {}^{32}S^{=} + \tfrac{1}{2}\,C\,{}^{34}S_2$$

is 1.019 at 25°C, (Tudge and Thode, 1950).

Dunford et al (1957) studied the ${}^{32}S \leftrightarrow {}^{34}S$ isotope exchange between sulphur dioxide and 100% sulphuric acid over the temperature range 200° to 400°C. They

have reported equilibrium constants of 1.014, 1.011 and 1.008 at 205°, 300° and 400°C respectively favouring the ^{34}S in the sulphuric acid. These results agree reasonably well with theoretical calculations made for the exchange between sulphate ion and sulphur dioxide in the reaction

$$^{34}SO_2 + {}^{32}SO_4^{=} = {}^{32}SO_2 + {}^{34}SO_4^{=}$$

Cragg(1961) reacted elemental sulphur with water in the temperature range 600°C to 1000°C to produce H_2S and SO_2. He then measured the isotopic composition of these products. Whereas the exchange between H_2S and SO_2 does not proceed at a noticeable rate directly, the presence of S^o permits exchange i.e. a S-atom can go from H_2S to S^o and then to SO_2 or vice versa. The isotope effects were quite small at these temperatures (2.5‰ enrichment of ^{32}S in H_2S as compared to SO_2 at 1000°C) and the measured values were slightly greater than the theoretical predictions. It was concluded that the discrepancy arose in the theoretical calculations because of the problem of assessing anharmonicity effects.

TABLE II

Reactants	Temp. (°C)	Experimental Conditions	Half-Time of Exchange	Literature Cited
$(HSS^*)^-$	90 100	0.01 mole S dissolved in aq. sol'n. containing 0.01 mole $(NH_4)_2S$	< 15 m	Voge (1939 Voge and Libby (1937)
$S^*O_3 \Leftrightarrow SO_2$	280	Equal volumes SO_2(g) and SO_3(g), total p ~ 76 cm.	> 12 d	Voge (1939)
	335	Equal volumes SO_2(g) and SO_3(g), total p ~ 76 cm.	~4.3 d	Voge (1939)
	280	Equal volumes SO_2(g) SO_3(g), and H_2O(g), total p ~ 76 cm.	~8.5 d	Voge (1939)
	280	Equal volumes SO_2(g), SO_3(g), and H_2O(g), total p ~ 76 cm.; platinized asbestos catalyst.	$\geq$ 25 h	Voge (1939
$SO_4^{*=} \Leftrightarrow HS^-$	100	Alk soln.	> 40 d	Voge (1939) Voge and Libby (1937)

TABLE II (continued)

Reactants	Temp. (°C)	Experimental Conditions	Half-Time of Exchange	Literature Cited
$S^*O_4^= \leftrightarrow SO_3^=$	100	Acid or Alk Soln.	> 40 d	Voge and Libby (1937)
$S^*SO_3^=$	Hot	Alk Soln.	> 1 h	Anderson (1936)
$S^*SO_3^= \leftrightarrow SS^*O_3^=$	125	Alk Soln. sealed in glass tubes	> 75 h	Ames (1951)
$S_2O_3^= \leftrightarrow HS^{*-}$	100	1 f NaOH	∿ 10 h	Voge (1939) Voge and Libby (1937)
$S_2O_3^= \leftrightarrow S^*O_3^=$	57	1 f NaOH	∿ 1 h	Voge (1939)
	100	1 f NaOH	< 1 h	Voge (1939)
	62	0.0650 f $Na_2S_2O_3$, 0.0719 f Na_2SO_3, 1.737 f NaCl, pH 5.0	137 ± 14 m	Ames (1951)
	96.2	0.0650 f $Na_2S_2O_3$, 0.0719 f Na_2SO_3, 1.737 f NaCl, pH 5.0	17.4 ± 1.7m	Ames (1951)
	88.9	0.0642 f $Na_2S_2O_3$, 0.2132 f Na_2SO_3, 1.208 f NaCl, pH 12.8	10.3 ± 1.0m	Ames (1951)
	88.9	0.0647 f $Na_2S_2O_3$, 0.2140 f Na_2SO_3, 0.21 f NaCl, pH 12.0	21.8 ± 2.2m	Ames (1951)

TABLE II (continued)

Reactants	Temp. (°C)	Experimental Conditions	Half-Time of Exchange	Literature Cited
$S_2O_3^{=} \leftrightarrow S^*O_3^{=}$	88.9	0.1198 f $Na_2S_2O_3$, 0.0620 f Na_2SO_3, 1.446 f NaCl, pH 12.7	15.1 ± 1.5m	Ames (1951)
	88.9	0.1164 f $Na_2S_2O_3$, 0.0592 f Na_2SO_3, 1.566 f NaCl, pH 5.9	19.4 ± 1.9m	Ames (1951)
$S_2Cl_2 \leftrightarrow S_8^*$	98.3	0.0319 f S_8 in S_2Cl_2(l)	∿ 30 m	Cooley and Yost (1940)
$CS_2 \leftrightarrow S_8^*$	100	0.05 f S_8 in CS_2(l)	>195 d	Cooley et al (1939)
$CS_2 \leftrightarrow H_2S^*$	120	0.108 f CS_2, 0.00 42 f H_2S in benzene	>275 d	Douglas et al (1949)
Thiourea$\leftrightarrow HS^-$	100		> 3 d	Tuck (1939)

Where appropriate, detailed information from the above studies will be incorporated in the discussion of results in this thesis.

CHAPTER V

CHEMISTRY OF SULPHUR

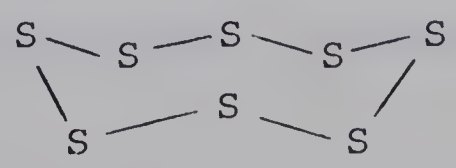
OCCURENCE:

Sulphur occurs widely in nature as elemental sulphur, hydrogen sulphide and sulphide ores, sulphur dioxide, sulphates and in complex organic molecules.

ELEMENTAL SULPHUR:

The structural relationships of sulphur are complex in each of the three phases, solid, liquid and gas. Despite a sufficient amount of study, many uncertainties and contradictions are found in literature. Some of the more important facts are the following:

There are two common crystalline modifications of sulphur. One is the rhombic form which is stable at room temperature while the other is formed from rhombic sulphur at 95.6°C by a very slow process and is called monoclinic sulphur. Both the forms of sulphur contain S_8 cyclic molecules. The rhombic crystals are built up from 8-membered rings of S atoms with S-S-S bond lengths of 2.12 Å.U and bond angles of 105.4°. According to Warren and Burwell (1935) the 8-membered rings of sulphur atoms are of the form shown below:



A third crystalline modification of sulphur, called Engel's sulphur has S_6 rings and can be obtained by pouring an $Na_2S_2O_3$ solution into concentrated HCl at 0°C and extracting with toluene. Plastic or amorphous sulphur is obtained by quickly quenching liquid sulphur which has been heated to 160°C or more.

The electronic configuration of sulphur is $1s^2 2s^2 2p^6 3s^2 3p^4$ and is such that the valency shell is two electrons short of the next noble gas configuration. The noble gas configuration can be attained by formation of the dinegative ion S^{2-}. However for sulphur the dinegative ion is less important and ionic sulphides are formed by the more basic cations. Since sulphur falls far below oxygen in electronegativity, the tendency is for covalency rather than electrovalency, with formal oxidation states +2, +4 and +6 as the important states. The binary compound with hydrogen (H_2S) is a simple example of the many compounds in which sulphur atoms are 2-covalent. The existence of more than one oxidation state of sulphur is attributed to the availability of d orbitals in the valency shell of the sulphur atom, which permits this element to attain excited configurations corresponding to oxidation states of +4 (four unpaired electrons) and +6 (six unpaired electrons), as shown:

	3s	3p	3d	
Ground State	↑↓	↑↓↑↑		
1st excited State	↑↓	↑ ↑↑	↑	+4 State
2nd excited State	↑	↑ ↑↑	↑↑	+6 State

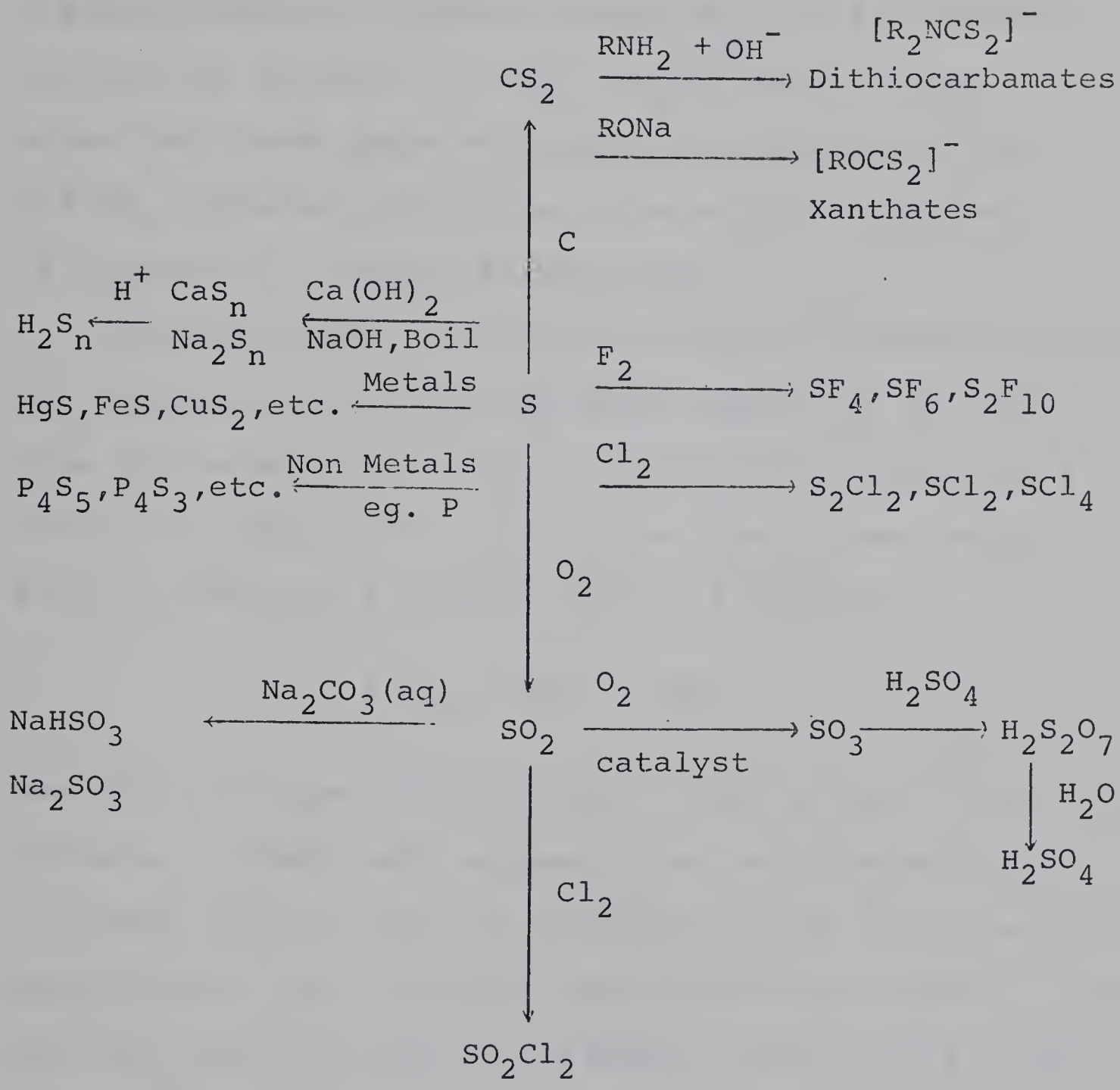
These higher oxidation states are most commonly found in the compounds formed by combination with highly electronegative elements like oxygen and fluorine, e.g. SO_2, SF_4, SO_3 and SF_6.

REACTIONS OF ELEMENTAL SULPHUR:

Sulphur is a moderately reactive substance. It combines directly with halogens and with a number of metals and non metals. Sulphur is not attacked by nonoxidizing acids. It is attacked on heating with concentrated sulphuric acid or nitric acid. Sulphur dissolves in fuming sulphuric acid giving yellow to blue solutions which contain as yet unidentified paramagnetic species. Sulphur also dissolves to a very limited extent in aqueous solutions of its anions S^{2-}.

Sulphur reacts with many organic molecules as well. For example, saturated hydrocarbons are dehydrogenated. The reaction of sulphur with olefins is technically very important, because of its wide use in the vulcanization (formation of sulphur bridges between chains) of natural and synthetic rubbers. Some of the important reactions

of sulphur are depicted below (after Cotton and Wilkinson, 1962):



OXIDES OF SULPHUR:

The principal oxides of sulphur are the dioxide, SO_2, and trioxide SO_3; there also exist the oxides S_2O and SO_4. The lower oxide is produced for example when a glow discharge is passed through SO_2 and for several decades was thought to be SO. Recent studies have shown that these gases are equimolar mixtures of S_2O and SO_2. S_2O is believed to have the structure SSO and is unstable at ordinary temperatures.

Sulphur dioxide results when sulphur or metal sulphides are roasted in air, although small amounts of SO_3 also form in the burning process. The liquid (boiling point - 10°C) is a good solvent and at one time it was thought that it undergoes a process of self ionization.

$$2\ SO_2 = SO^{2+} + SO_3^{2-}$$

But this now seems doubtful due to lack of any direct evidence. Recent work suggests that self ionisation if it occurs at all, plays no significant role in the solvent properties of SO_2. Sulphur dioxide is very soluble in water and the resulting solution is weakly acidic owing to the equilibrium:

$$SO_2 + 2\ H_2O = H_3O^+ + HSO_3^-$$

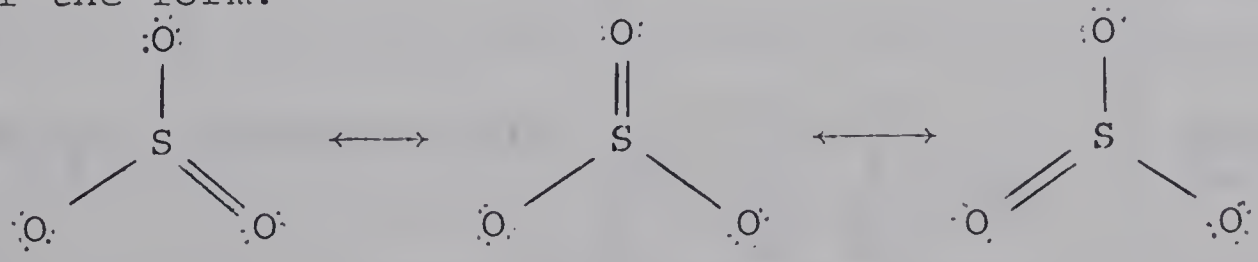
In the structure of sulphur dioxide, the two oxygen

atoms are bonded to the sulphur atom and the bond angle is 119.5°. Gaseous SO_2 molecules are bent and symmetrical. The short S-O bond distance implies considerable multiple bonding. The bonding is presumably of the resonant forms:



Sulphur dioxide solidifies to form a molecular lattice as far as is known.

Sulphur dioxide is used in H_2SO_4 production. It is used as a reducing agent, although it is not a powerful one except in basic solution where sulphide ion is formed. Of the trioxide only sulphur trioxide, SO_3 is of importance. It is produced when sulphur dioxide combines with oxygen, but the reaction is very slow unless a catalyst is used. Platinum sponge, vanadium pentoxide (V_2O_5), and nitric oxide (NO) serve as good catalysts under various conditions. SO_3 reacts vigorously with water to form sulphuric acid, H_2SO_4 which is a very powerful oxidising agent. The free molecule as it occurs in the gas phase, has a planer, triangular structure involving S-O bonding of very short bond length of 1.43 Å.U. The structure of the free molecule of SO_3 is of the form:

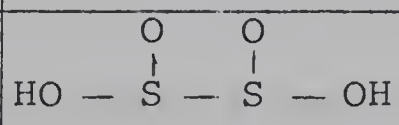
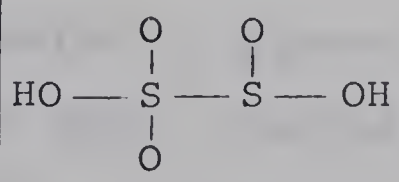
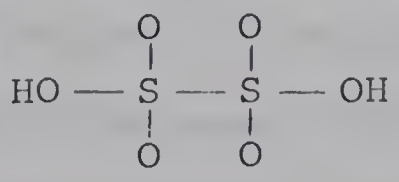


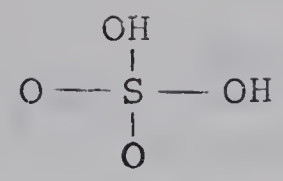
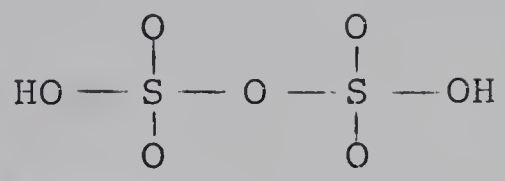
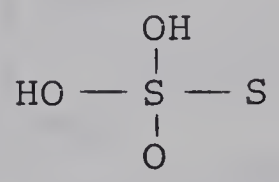
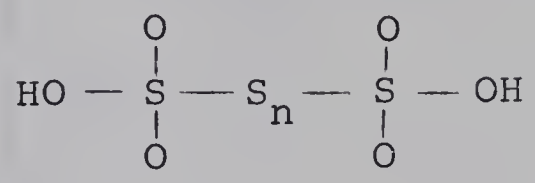
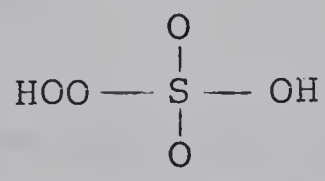
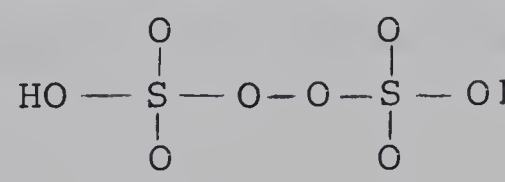
The solid SO_3 is however, complex from the structural point of view and at least three well defined phases are known.

OXYACIDS OF SULPHUR:

Sulphur form oxyacids which are very important and numerous. Some of the acids are not actually known as such, but occur only in the form of their anions and salts. The acids are classified according to the oxidation state of the central sulphur atom. In Table III, various oxy-acids of sulphur are structurally grouped (after Cotton and Wilkinson, 1962; and Duffey, 1966).

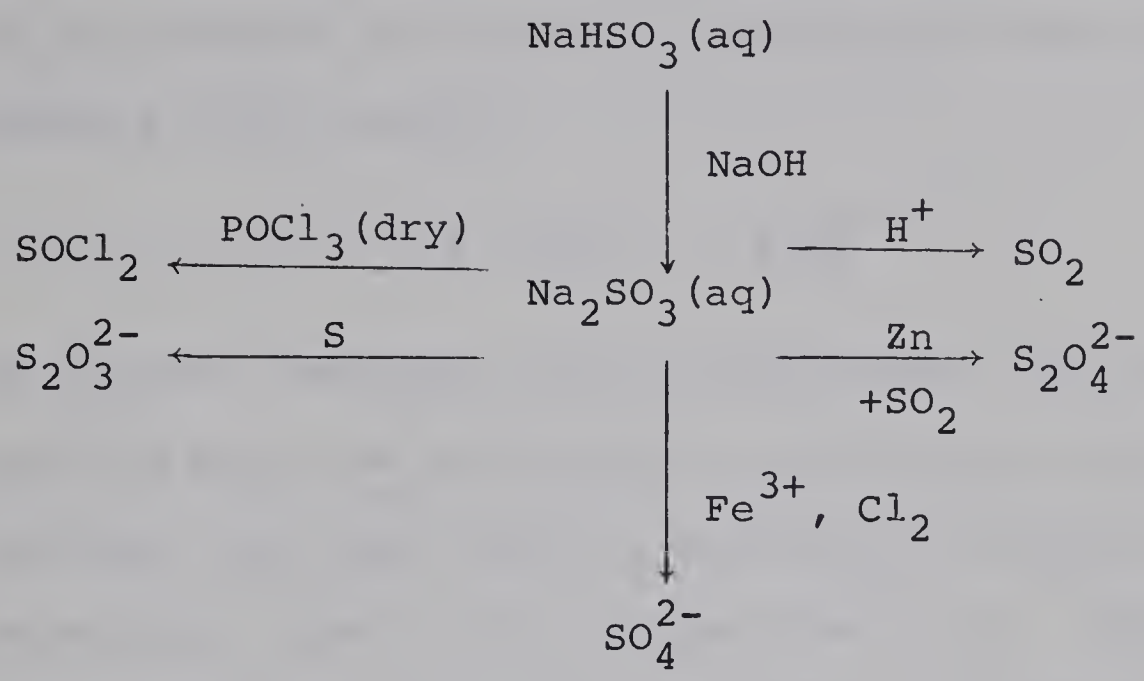
TABLE III

Oxidation State of S-atom	Formula	Name	Structure	Comments
+2	H_2SO_2	Sulphoxylic Acid (free acid unknown)	HO — S — OH	
+3	$H_2S_2O_4$	Dithionous Acid (free acid unknown)		Both S-atoms are equivalent.
+4	H_2SO_3	Sulphurous Acid	SO_3^{2-} (in sulphites)	
	$H_2S_2O_5$	Pyrosulphurous Acids (free acids unknown)		Mean oxidation number is +4 although S-atoms are not equivalent.
+5	$H_2S_2O_6$	Dithionic Acid		Both S-atoms are equivalent.

+6	H_2SO_4	Sulphuric Acid		
	$H_2S_2O_7$	Pyro-(ordi-) Sulphuric Acid		Both S-atoms are equivalent.
	$H_2S_2O_3$	Thiosulphuric Acid		The sulphur atoms are not equivalent.
	$H_2S_nO_6$	Polythionic Acids		N > 3 bridging S-atom is regarded as a dinegative ligand.
	H_2SO_5	Peroxymono-sulphuric Acid		
	$H_2S_2O_8$	Peroxydi-sulphuric Acid		Both S-atoms are equivalent.

Although sulphurous acid itself does not exist, two series of salts, the bisulphites HSO_3^-, and the sulphites containing SO_3^{2-}. are well known. There is unequivocal evidence of SO_3^{2-} ion in crystals; it appears that in dilute solution, the principal ion is $HOSO_2^-$, whereas at higher concentrations, HSO_3^- and $S_2O_5^{2-}$ are the major species. X-ray studies of Na_2SO_3 has shown that SO_3^{2-} ion is of pyramidal structure. Some important reactions of sulphites are shown below (after Cotton and Wilkinson, 1962).

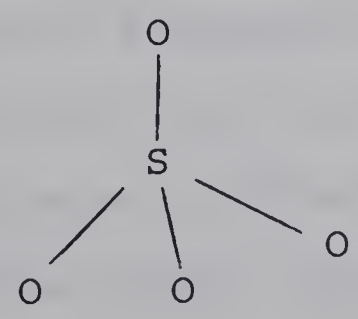
$$SO_2 + Na_2SO_3 \xrightarrow{\text{cold}} NaHSO_3(aq) \xrightarrow[\text{in excess}]{SO_2} Na_2S_2O_5$$



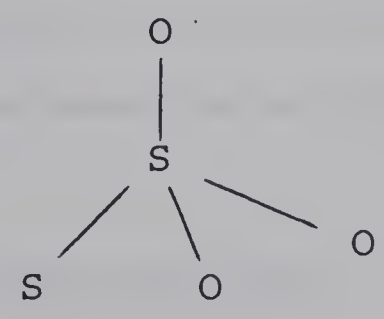
As evident in the above reaction scheme, the thiosulphates are made by boiling sulphite solutions with sulphur:

$$SO_3^{2-} + S \longrightarrow S_2O_3^{2-}$$

Thiosulphates are numerous, fairly stable and usually very soluble in water. The $S_2O_3^{2-}$ ion is structurally analogous to the sulphate, SO_4^{2-} ion.



(SO_4^{2-}) ;

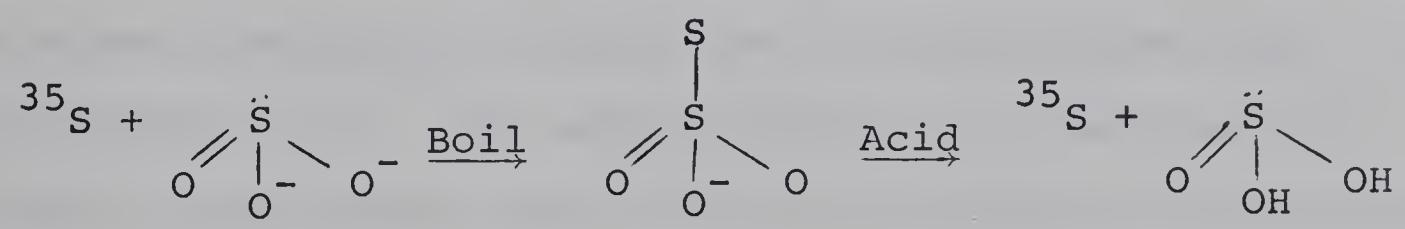


$(S_2O_3^{2-})$

Thus the thiosulphate ion, $S_2O_3^{2-}$, may be regarded as derived from the sulphate ion, SO_4^{2-}, by the replacement of an oyxgen atom by sulphur. Alkali metal thiosulphates may be prepared by boiling a solution of the corresponding sulphite with sulphur:

$$S + SO_3^{2-} \longrightarrow S_2O_3^{2-}$$

The reverse reaction, to give sulphurous acid and sulphur, occurring when the thiosulphate solution is acidified. These reactions have been used to establish non-equivalence of the sulphur atoms in the thiosulphate ion. Hence, if thiosulphate prepared from sulphite and labelled sulphur i.e. sulphur containing the radioactive isotope ^{35}S, is acidified, the precipitated sulphur carries the entire radioactivity:



If the sulphur atom in the thiosulphate ion occupied structurally equivalent positions, the radioactivity would be expected to distribute itself between the sulphur and the sulphurous acid solution.

Neyman (1952) used $H_2\,^{35}S$ in the reaction:

$$4\ SO_2 + 2\ H_2S + 6\ NaOH \rightarrow 2\ Na_2S_2O_3 + 5\ H_2O$$

All the central S-atoms of $S_2O_3^{2-}$ ions came from SO_2, but the ligand atom partly from SO_2 and partly from H_2S. Addition of acid to thiosulphate solution does not cause decomposition until pH of 4.6 is reached. The $HS_2O_3^-$ ion then formed, being much less stable than the $S_2O_3^{2-}$ ion, decomposes quickly:

$$H S_2 O_3^- \rightarrow H SO_3^- + S$$

Thus the thiosulphates exist only as neutral salts.

Pure sulphuric acid (referred to as 100 per cent sulphuric acid) can be made by adding pyrosulphuric acid to the ordinary concentrated acid which is roughly 98 per cent H_2SO_4 by weight. The pure acid melts at 10.36°C and boils at 317°C. Sulphuric acid has a great affinity for water and is a very powerful acid. Many substances experience a high degree of protonation when dissolved in it. The self-ionisation of the liquid is rather complicated, but involves essentially autoprotonation and autodehydration:

$$2\ H_2SO_4 = H_3SO_4^+ + HSO_4^-$$

$$2\ H_2SO_4 = H_3O^+ + HS_2O_7^-$$

Sulphates and acid sulphates of virtually all electropositive elements are known and most of them are soluble in water.

When acid sulphates are heated, pyrosulphate ions are formed with the liberation of water in the first instant:

$$2\ M\ HSO_4 \xrightleftharpoons{Heat} M_2S_2O_7 + H_2O$$

Further heating derives off SO_3 to leave the sulphate.

Pure sulphuric acid contains a number of species in equilibrium:

$$2\ H_2SO_4 = H_2O + H_2S_2O_7$$

$$H_2SO_4 + H_2O = H_3O^+ + HSO_4^-$$

$$H_2SO_4 + H_2S_2O_7 = H_3SO_4^+ + HS_2O_7^-$$

$$2\ H_2SO_4 = H_3SO_4^+ + HSO_4^-$$

SULPHIDES AND POLYSULPHIDES:

Most metals form sulphides, and when these compounds are treated with acid they yield the hydrogen compound H_2S. Aqueous solutions of the polysulphides are feebly acidic, the acid strength increasing with decreasing bond strength of the hydride, (increasing no. of sulphur atoms). Hydrogen sulphide dissolves in water to a moderate extent to give a slightly acidic solution. Its dissociation equilibria in water are:

$$H_2S + H_2O = H_3O^+ + HS^-, \qquad k = 1 \times 10^{-7}$$

$$HS^- + H_2O = H_3O^+ + S^{2-}, \quad k \sim 10^{-14}$$

Sulphides of the alkali metals and alkaline earth metals are ionic compounds, but owing to the weakness of the parent acid they undergo extensive hydrolysis in solution:

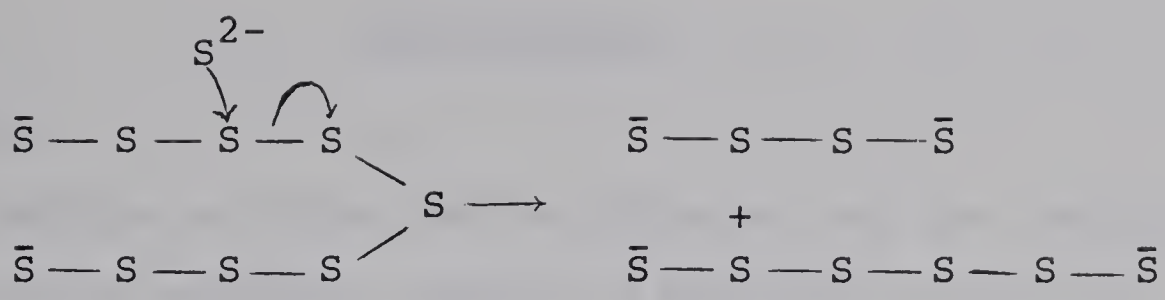
$$S^{2-} + H_2O = OH^- + HS^-$$

$$HS^- + H_2O = OH^- + H_2S$$

The solutions dissolve sulphur with the formation of polysulphide ions which have the general formula S_n^{2-}. Hydrogen polysulphides, or sulphanes (general formula H_2S_n, n = 1,2,3,4,5,6) can be obtained as yellow oils by acidification of the metal polysulphide. The formation of polysulphides may be visualised as resulting from the nucleophilic attack of a sulphide ion upon the S_8 ring, leading initially to the formation of S_9^{2-} open chain anion:



The curved arrows represent electron shifts occuring during the reaction. Further attack by sulphide ion at various points in the S_9^{2-} chain gives a mixture of smaller doubly charged sulphur chains, e.g.



In alkaline solution, the hydrogen polysulphides readily decompose to yield free sulphur and the sulphide ion, S^{2-}.

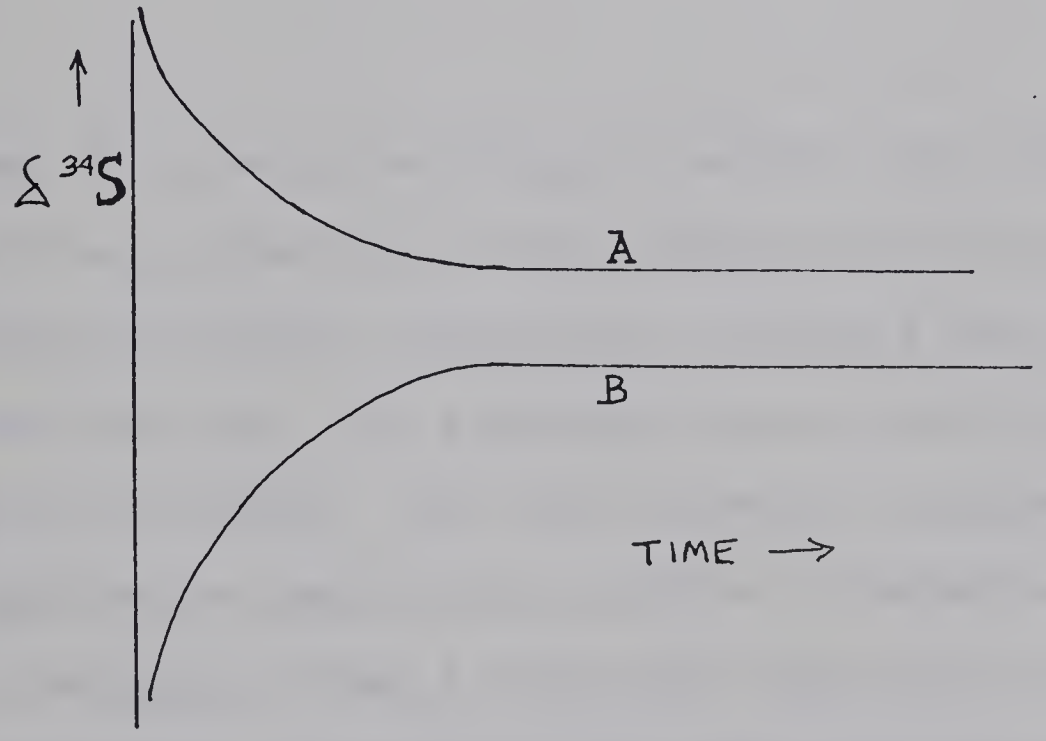
CHAPTER VI

EXPERIMENTAL

GENERAL:

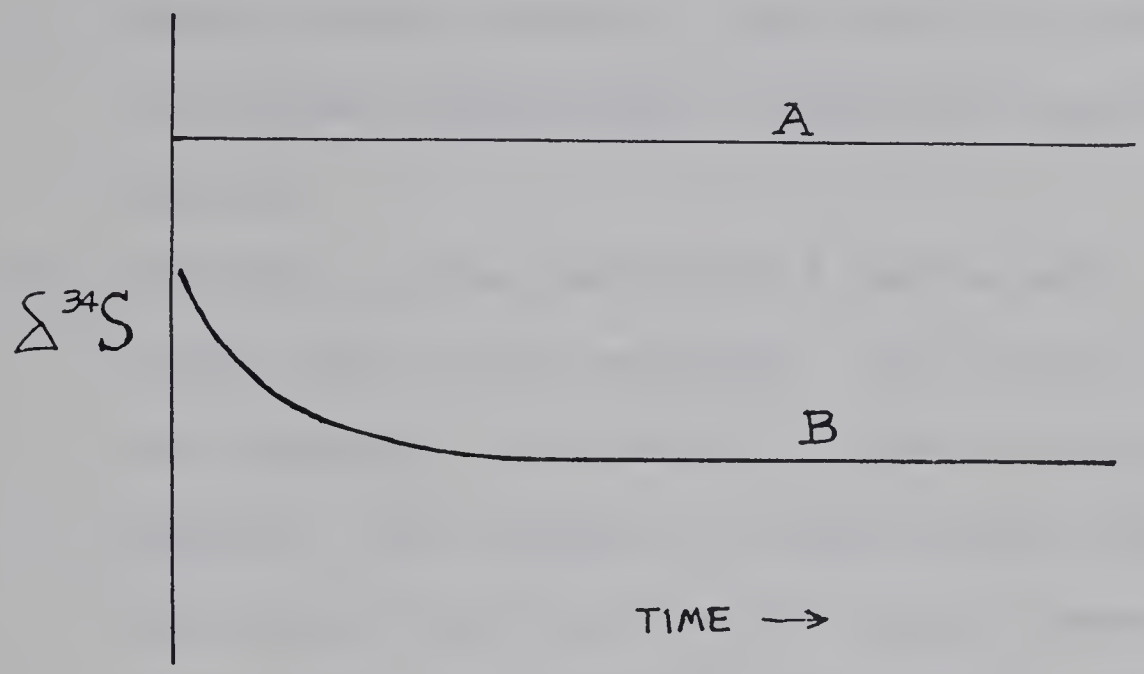
Isotope exchange can be detected and the isotopic equilibrium exchange constant K measured using mass spectrometry and reactants of normal isotopic composition. Further, one can observe the establishment of equilibrium by plotting the $\delta\ ^{34}S$ values of the reaction components against reaction time.

The establishment of equilibrium during a reaction between two isotopic species A and B might resemble the plots shown below.



However, if one of the components A is much more abundant than that of B, experimentation may be simplified. Since the net isotopic composition of the system must remain constant, the isotopic composition of the more abundant

component A changes very little compared with that of B. Hence the experimental plots should behave typically as follows:



Now, it is only necessary to monitor the $^{34}S/^{32}S$ ratio of B as a function of time instead of making measurements for the isotopic composition of both A and B as in the previous case. If exchange occurs, the isotopic composition of B is altered. The rate at which B proceeds to its equilibrium composition provides information on the rate of exchange. When B ceases to alter in its isotopic composition, equilibrium has been achieved and the isotopic exchange equilibrium constant K can then be measured. This experimental technique has numerous advantages:

(i) The experiments can be conducted with relatively inexpensive commercial reactants whereas radioactively

labelled compounds are expensive and more difficult to handle.

(ii) There is no time limitation, as in the case of radioactive tracer studies. The reactants can be left in contact indefinitely to examine long term equilibrations.

(iii) The shape of the curve for B can be used to calculate a half time of the exchange. This data is useful for commercial separation of isotopes using exchange methods. For example, in multi-plate exchange columns, one should know the time of contact necessary to effect exchange and design the length, number of plates, and flow rates accordingly.

(iv) Since isotope ratios can be compared with a standard deviation and reproducibility of $\pm$ 0.01 per cent mass spectrometrically, the measurement errors are much smaller than those of the radioactive studies.

There are also limitations with this technique.

(i) Sometimes, exchange can occur without a measurable isotope effect. In this case, the radioactive tracer technique would permit an unambiguous answer.

(ii) Confusion may arise if A and B are isotopically different by (K-1) prior to the start of the experiment.

(iii) The radioactive exchange technique is generally more sensitive in that very small amounts of the radioactive tracer can be detected in components.

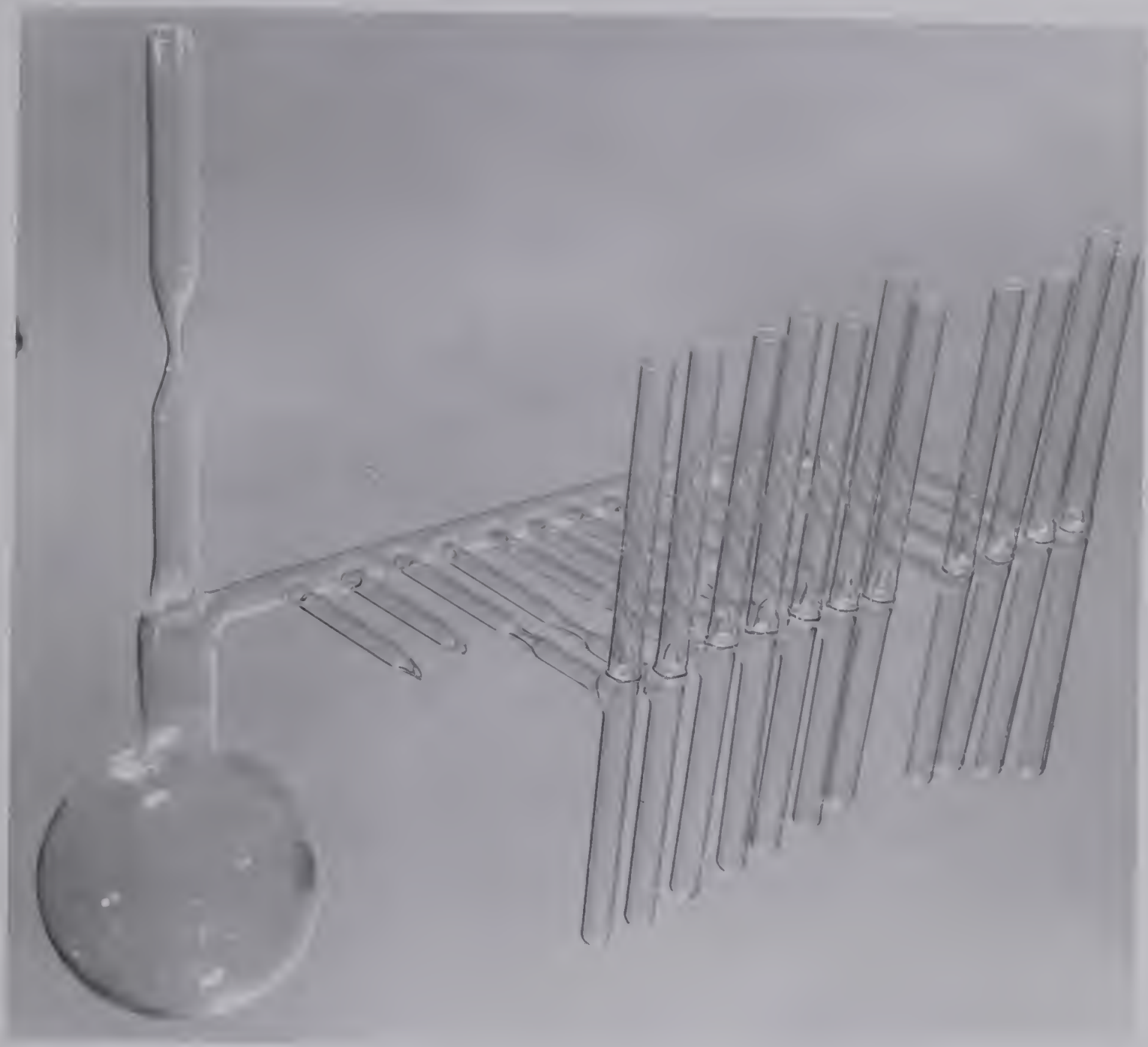
EQUILIBRATION EXPERIMENTS: PREPARATION OF SAMPLES

The reaction flask used in the experiments is shown in Figure IV. 500 ml pyrex glass flasks were fitted with a number of glass break seal tubes and a long neck with a constriction. After washing and drying in an oven, about 100 ml of the solution for exchange study were added to the reaction vessel which was then mounted on a vacuum line. The flask was then evacuated with care being taken not to boil the solution vigorously. In some cases, this required the placement of a cold bath around the flask. The object in this step was to remove oxygen from the solution which might interfere with the exchange. In some studies,oxygen was purposely introduced in order to study its effect. The gas of interest was introduced from a laboratory cylinder into the reaction flask to the desired pressure. (The total pressure of the system had to be less than atmospheric at the temperature studied in order to provide break seal removal). After filling, the reaction flask was taken from the vacuum line by fusing the constriction. The reaction flask was then placed in an oven at the desired temperature. Break seal tubes of

FIGURE IV

Reaction flask for equilibrating

liquid and gas components



the gaseous components were removed from the reaction flask at different time intervals. In some studies, liquids and solids were simply mixed in open containers and capped. The solid and liquid states were sampled from time to time.

All samples were converted to SO_2 for mass spectrometric analyses as follows:

(1) SO_2 gas constituents were analyzed directly.

(2) Elemental sulphur was burned in a purified oxygen stream at 1200°C.

(3) Sulphides were precipitated as CdS, converted to Ag_2S in $AgNO_3$ solution, and then combusted as in (2).

(4) Sulphates, sulphites, thiosulphates, etc. were reduced to H_2S in a reflux column with a reducing mixture of HI, HCl and H_3PO_2 as described by Harrison and Thode (1957). The H_2S was trapped as CdS and processed as in (3).

The combustion furnace and sample purification procedures have been previously described by Husain (1965).

MASS SPECTROMETRY:

The mass spectrometer used was a 12 inch radius, 90° magnetic analyzer featuring simultaneous collection of masses 64 and 66 and digital recording as described by McCullough and Krouse (1965). A standard and an unknown

sample could be alternately introduced into the mass spectrometer by a magnetic valve system. During the three years in which data were obtained, this inlet system was altered many times. As a result, the reproducibility of the data over all of this time is more realistically ± 0.3‰ instead of the ± 0.1‰ usually claimed with this instrumentation. This deviation is nevertheless quite small in comparison to the isotopic variations measured.

The sample handling line for the mass spectrometer has been previously described (Husain, 1965).

CHAPTER VII

RESULTS OF EXPERIMENTAL $^{32}S \longleftrightarrow ^{34}S$ EXCHANGE STUDIES

It is interesting to note that the laboratory reagents exhibited large variations in their $^{34}S/^{32}S$ abundance ratios as shown in Table IV. All $\delta^{34}S$ values are relative to the meteoritic troilite reference.

TABLE IV

$^{34}S/^{32}S$ Composition of Reagents

REAGENT	$\delta^{34}S$
H_2SO_4	-0.6
SO_2	+1.6
Na_2SO_4	+8.6
$NaHSO_3$	+2.8
$Na_2S_2O_3$	+10.9
Ligand S-atom of S_2O_3	+9.9
Central S-atom of S_2O_3	+8.8
H_2S	+22.6
S^0 (powder)	-2.3
Na_2S	+1.0
Na_2SO_3	+0.4

EXCHANGE BETWEEN H_2SO_4 and SO_2:

Sulphur isotope exchange between reagent grade 95.5 to 96.5% H_2SO_4 (Nichols Chem. Co. Ltd.) and SO_2 gas was studied using the equilibration flask previously described (Figure IV). The experiments were carried out at various temperatures in the range 100°C to 265°C. In some experiments, the effects of SO_2 pressure and the presence of O_2 were also examined. These results are summarized in Tables V to XVII, Figures V to XVII and Figures V-a to XVII-a. The series designation refers to the time sequence of experiments in the laboratory notebooks. Since a number of different equilibrations were carried out, the series designation will not be in sequence in this thesis.

In these studies, the H_2SO_4 was the dominant component (100 ml) and so its $^{34}S/32_S$ composition should have negligible variation throughout the experiments. Tables V to XVII present the mass spectrometric determinations, while Figures V to XVII show how the isotopic composition of the SO_2 varied with time. Figures V-a to XVII-a follow the method of analysis of Northrop and Clayton (1966) as discussed under theory. The calculations for these latter diagrams are given in the appendix. (Tables V-a to XVII-a).

EXCHANGE BETWEEN Na_2SO_4 AND SO_2:

Two experiments were conducted to determine the exchange between Na_2SO_4 and SO_2. In one case, solid anhydrous Na_2SO_4 was in contact with 200 mm Hg pressure of SO_2 at 240°C for 20 hours. These results are summarized in Table XVIII and Figure XVIII. In the second case, 12.2 gm Na_2SO_4 in 100 ml of H_2O were in contact with SO_2 for 159 days at 100°C. These results are compiled in Table XIX and Figures XIX and XIX-a.

EXCHANGE BETWEEN $NaHSO_3$ (IN SOLUTION) AND SO_2:

Two experiments were carried out to examine this exchange. In one (Table XX, Figures XX and XX-a), 50 ml 1N $NaHSO_3$ solution were equilibrated with 130 mm-Hg of SO_2 for 12 hours at 80°C. In the second case (Table XXI, Figures XXI and XXI-a), 50 ml 1N $NaHSO_3$ solution were in contact with 200 mm-Hg pressure of SO_2 for 23 hours at room temperature. In these experiments the $NaHSO_3$ solution was initially frozen in a dry ice bath and pumped upon to remove air. The SO_2 was introduced while the solution was still frozen. Thus the time for thermal equilibration with such aqueous solutions was longer than for other experiments.

EXCHANGE BETWEEN $Na_2S_2O_3$ (IN SOLUTION) AND SO_2:

One experiment was conducted in which 6 gm of sodium

thiosulphate dissolved in 25 ml of deionized water were in contact with 200 mm-Hg pressure of SO_2 for 6 days (Table XXII to XXV, Figures XXII and XXII-a). During this exchange a dark yellow precipitate formed almost immediately and after about 7 hours, the colour became yellowish white. Samples taken after 7 hours had very low SO_2 content (too low to obtain good mass spectrometric measurements).

EXCHANGE BETWEEN $Na_2S_2O_3$ (IN SOLUTION) AND H_2S:

Three experiments were conducted in which 6 gm of $Na_2S_2O_3$ in 25 ml of deionized water were in contact with SH_2 at 200 mm Hg pressure and at 21°C, 60°C and 80°C (Tables XXIII to XXV, Figures XXIII to XXV and XXIII-a to XXV-a). Again, in these experiments, elemental sulphur was produced almost immediately. However there was sufficient H_2S in all cases to permit mass spectrometric analyses.

EXCHANGE BETWEEN H_2SO_4 AND H_2S:

Two experiments were conducted in which 50 ml of H_2SO_4 in 150 ml of H_2O were in contact with 350 mm-Hg pressure of H_2S at room temperature and 60°C (Tables XXVI and XXVII). In both cases, H_2S content of the gas above the solution immediately decreased to a very low value, elemental sulphur and sufficient quantity of SO_2

formed. Therefore the isotopic composition of this SO_2 was monitored as a function of time.

EXCHANGES WITH ELEMENTAL SULPHUR:

Elemental sulphur in the form of a fine powder (Fisher Scientific Company, Lot. No. 731095) was placed in contact with the following solutions at 60°C and room temperature.

H_2SO_4	solution diluted 1:4
Na_2SO_4	(1.22 gm per 100 ml of H_2O)
Na_2SO_3	(6.20 gm per 100 ml of H_2O)
$Na_2S_2O_3$	(25 gm per 100 ml of H_2O)

Sulphur powder was sampled and washed and its isotopic composition determined as a function of time. These results are summarized in Table XXVIII.

TABLE V

Series A

Equilibration of H_2SO_4 and SO_2 at 265°C

(Initial SO_2 pressure = 10 mm of Hg)

$\delta^{34}S$ of Initial H_2SO_4 = -0.57

$\delta^{34}S$ of initial SO_2 = +1.59

Sample	Time of Exchange	$\delta^{34}S$ of SO_2
A-1	47 m	+1.41
A-2	1 h - 7 m	-0.44
A-3	1 h - 27 m	-2.76
A-4	1 h - 47 m	-4.71
A-5	2 h - 7 m	-5.63
A-6	2 h - 40 m	-6.26
A-7	5 h - 1 m	-9.94
A-8	9 h - 22 m	-10.71

TABLE VI

Series B

Equilibration of H_2SO_4 and SO_2 at 265°C

(Initial SO_2 pressure = 100 mm of Hg)

$\delta^{34}S$ of Initial H_2SO_4 = -0.57

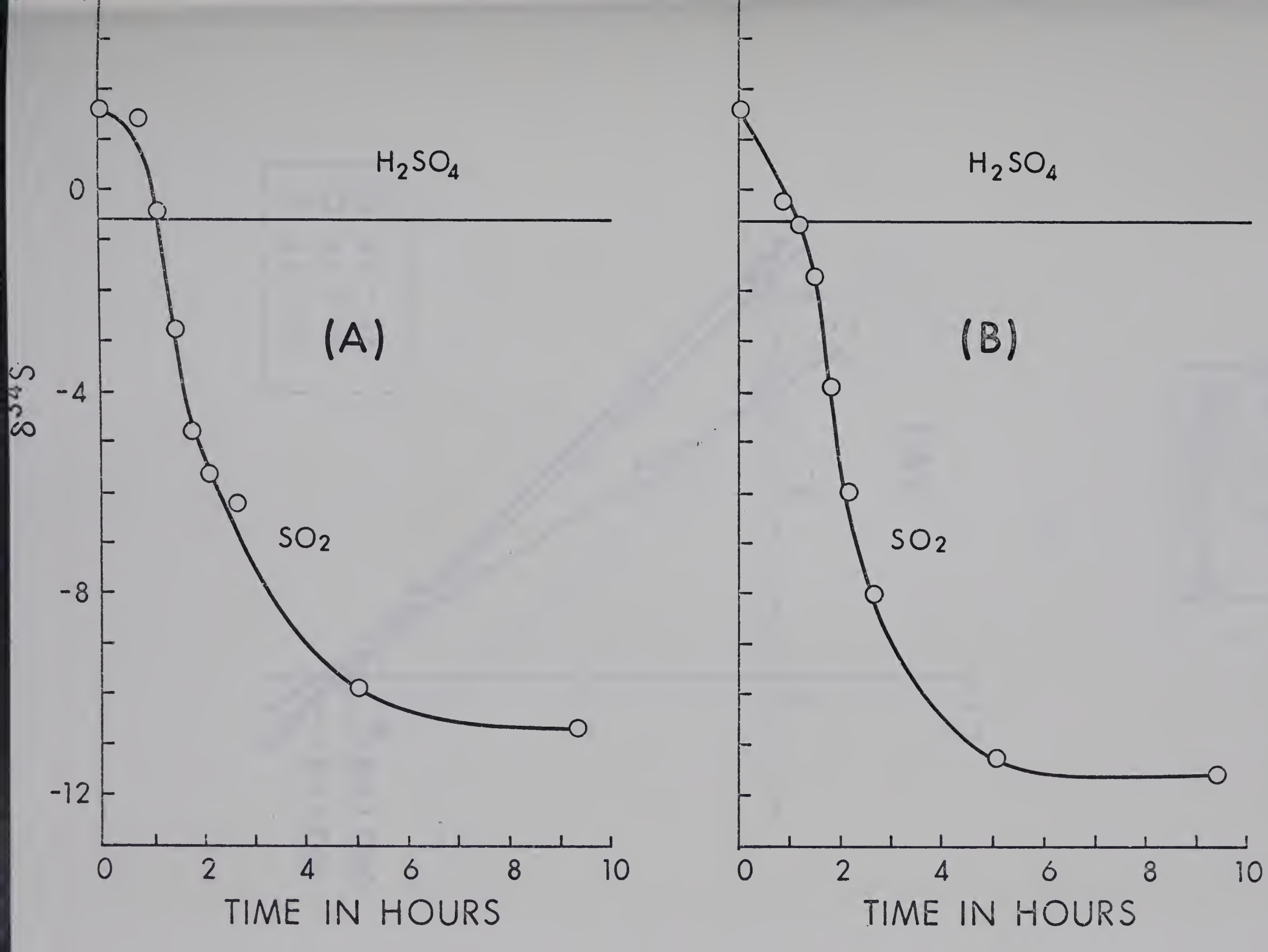
$\delta^{34}S$ of Initial SO_2 = +1.59

Sample	Time of Exchange	$\delta^{34}S$ of SO_2
B-1	49 m	-0.26
B-2	1 h - 9 m	-0.73
B-3	1 h - 29 m	-1.75
B-4	1 h - 49 m	-3.89
B-5	2 h - 9 m	-6.04
B-6	2 h - 39 m	-8.05
B-7	5 h	-11.30
B-8	9 h - 24 m	-11.55

FIGURES

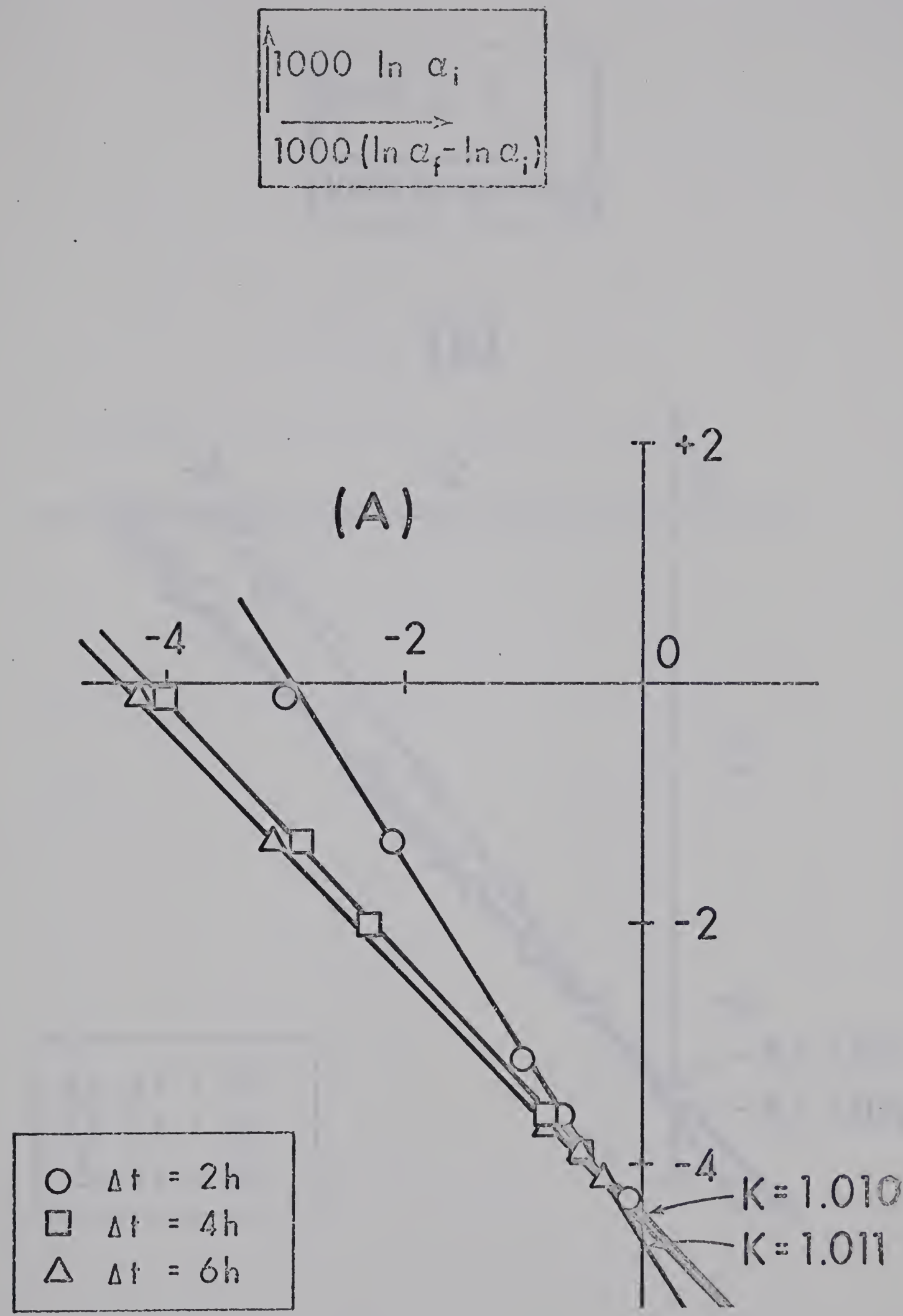
V and V-a: Series (A), Equilibration of H_2SO_4 and SO_2 at 265°C., SO_2 pressure 10 mm Hg.

VI and VI-a: Series (B), Equilibration of H_2SO_4 and SO_2 at 265°C., SO_2 pressure 100 mm Hg.


H_2SO_4
0
-4
-8
-12
$\delta^{34}S$
SO_2
(A)
0
2
4
6
8
10
TIME IN HOURS
H_2SO_4
(B)
SO_2
0
2
4
6
8
10
TIME IN HOURS






1000 ln α_i
1000 (ln α_f - ln α_i)
(A)
+2
-2
-4
-4
-2
0
K = 1.010
K = 1.011
○ Δt = 2h
□ Δt = 4h
△ Δt = 6h



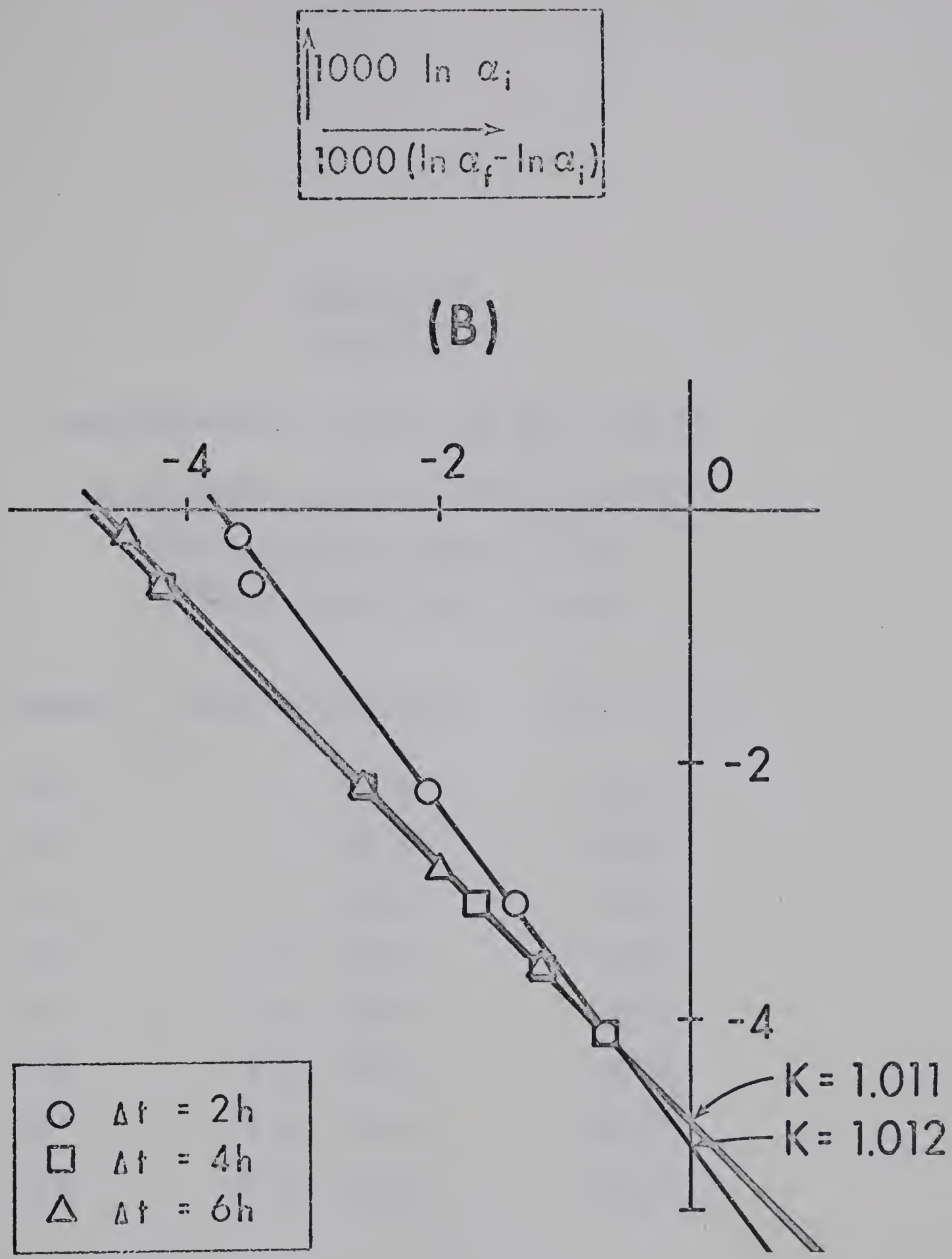

1000 ln α_i
1000 (ln α_f - ln α_i)
(B)
-4
-2
0
-2
-4
K = 1.011
K = 1.012
Δt = 2h
Δt = 4h
Δt = 6h



TABLE VII

Series C

Equilibration of H_2SO_4 and SO_2 at 265°C

(Initial SO_2 pressure = 200 mm of Hg)

$\delta^{34}S$ of Initial H_2SO_4 = -0.57

$\delta^{34}S$ of Initial SO_2 = +1.59

Sample	Time of Exchange	$\delta^{34}S$ of SO_2
C-1	18 m	+0.75
C-2	37 m	+0.69
C-3	57 m	-0.49
C-4	1 h - 17 m	-1.00
C-5	1 h - 47 m	-3.51
C-6	2 h - 57 m	-8.78
C-7	5 h - 47 m	-11.71
C-8	9 h - 14 m	-11.98

TABLE VIII

Series D

Equilibration of H_2SO_4 and SO_2 at 265°C

(Initial SO_2 pressure = 300 mm of Hg)

$\delta^{34}S$ of Initial H_2SO_4 = -0.57

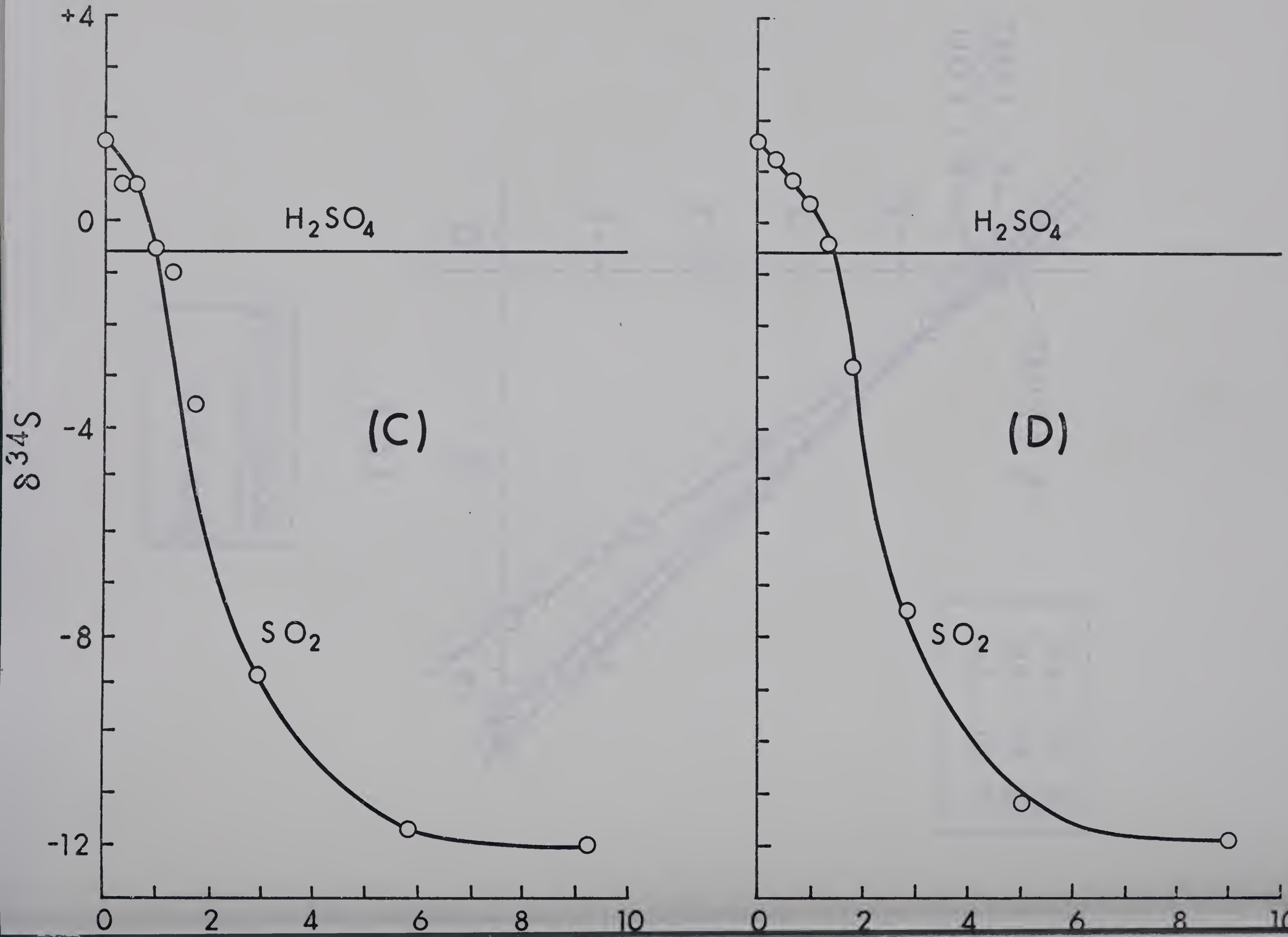
$\delta^{34}S$ of Initial SO_2 = +1.59

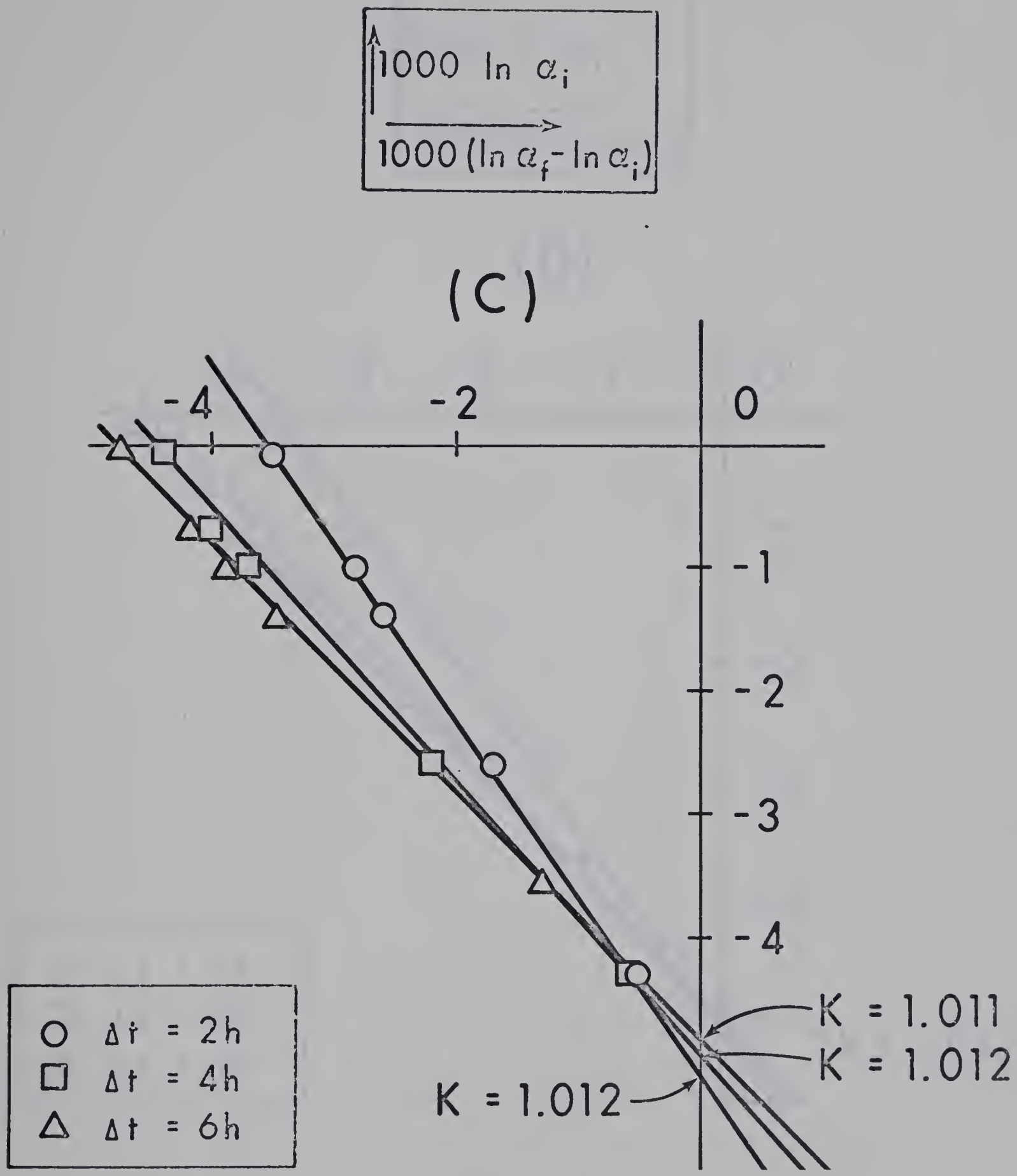
Sample	Time of Exchange	$\delta^{34}S$ of SO_2
D-1	20 m	+1.19
D-2	40 m	+0.83
D-3	1 h	+0.35
D-4	1 h - 20 m	-0.37
D-5	1 h - 50 m	-2.82
D-6	2 h - 50 m	-7.36
D-7	5 h	-11.18
D-8	9 h	-11.87

FIGURES

VII and VII-a: Series (C), Equilibration of H_2SO_4 and SO_2 at 265°C, SO_2 pressure 200 mm Hg.

VIII and VIII-a: Series (D), Equilibration of H_2SO_4 and SO_2 at 265°C, SO_2 pressure 300 mm Hg.


+4
0
-4
-8
-12
$\delta^{34}S$
H_2SO_4
SO_2
(C)
(D)
0
2
4
6
8
10


1000 ln α_i
1000 (ln α_f - ln α_i)
(C)
-4
-2
0
-1
-2
-3
-4
K = 1.011
K = 1.012
K = 1.012
○ Δt = 2h
□ Δt = 4h
△ Δt = 6h



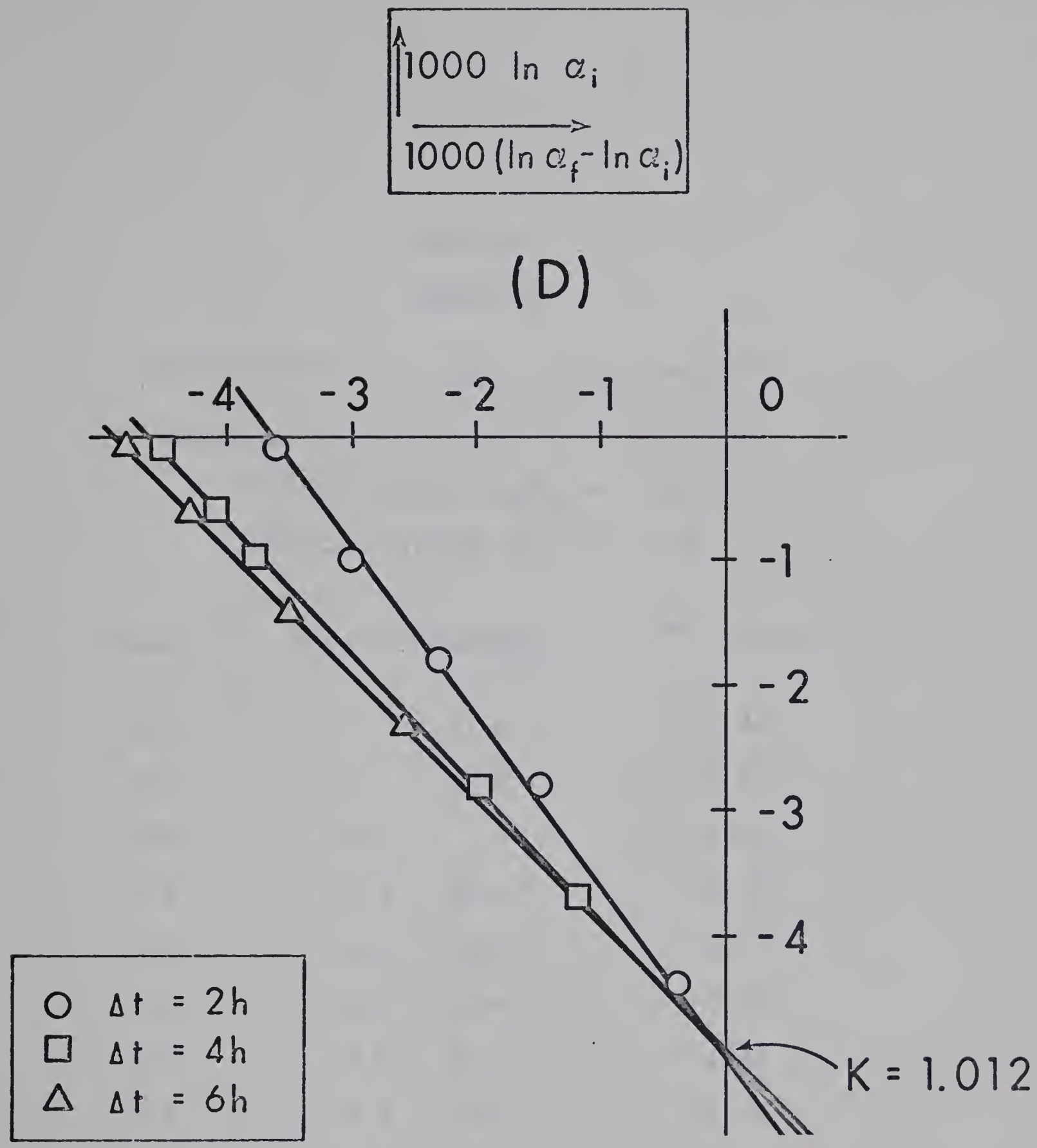

1000 ln α_i
1000 (ln α_f - ln α_i)
(D)
-4
-3
-2
-1
0
-1
-2
-3
-4
K = 1.012
○ Δt = 2h
□ Δt = 4h
△ Δt = 6h



TABLE IX

Series E

Equilibration of H_2SO_4 and SO_2 at 265°C

(Initial SO_2 pressure = 400 mm of Hg)

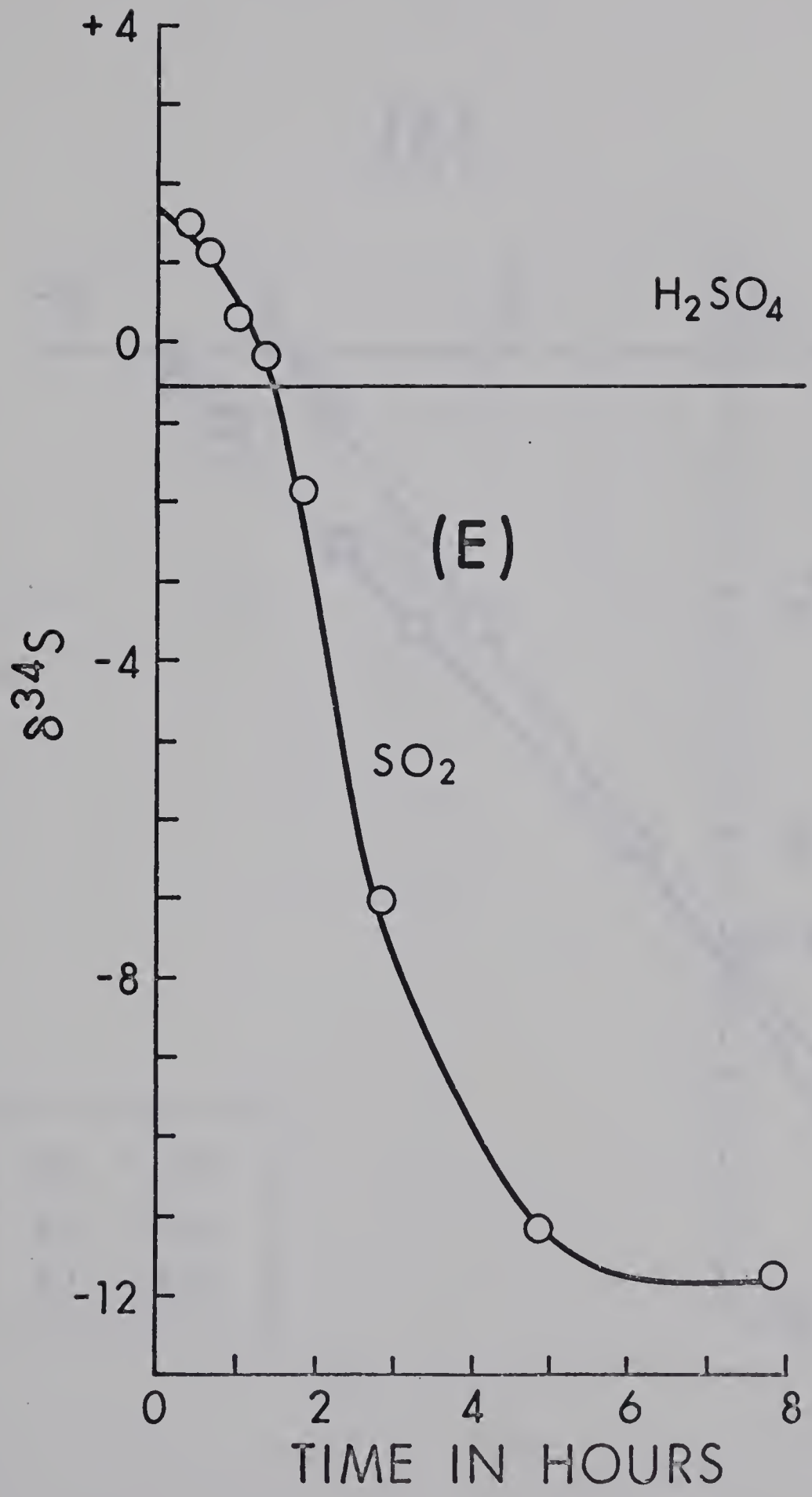
$\delta^{34}S$ of Initial H_2SO_4 = -0.57

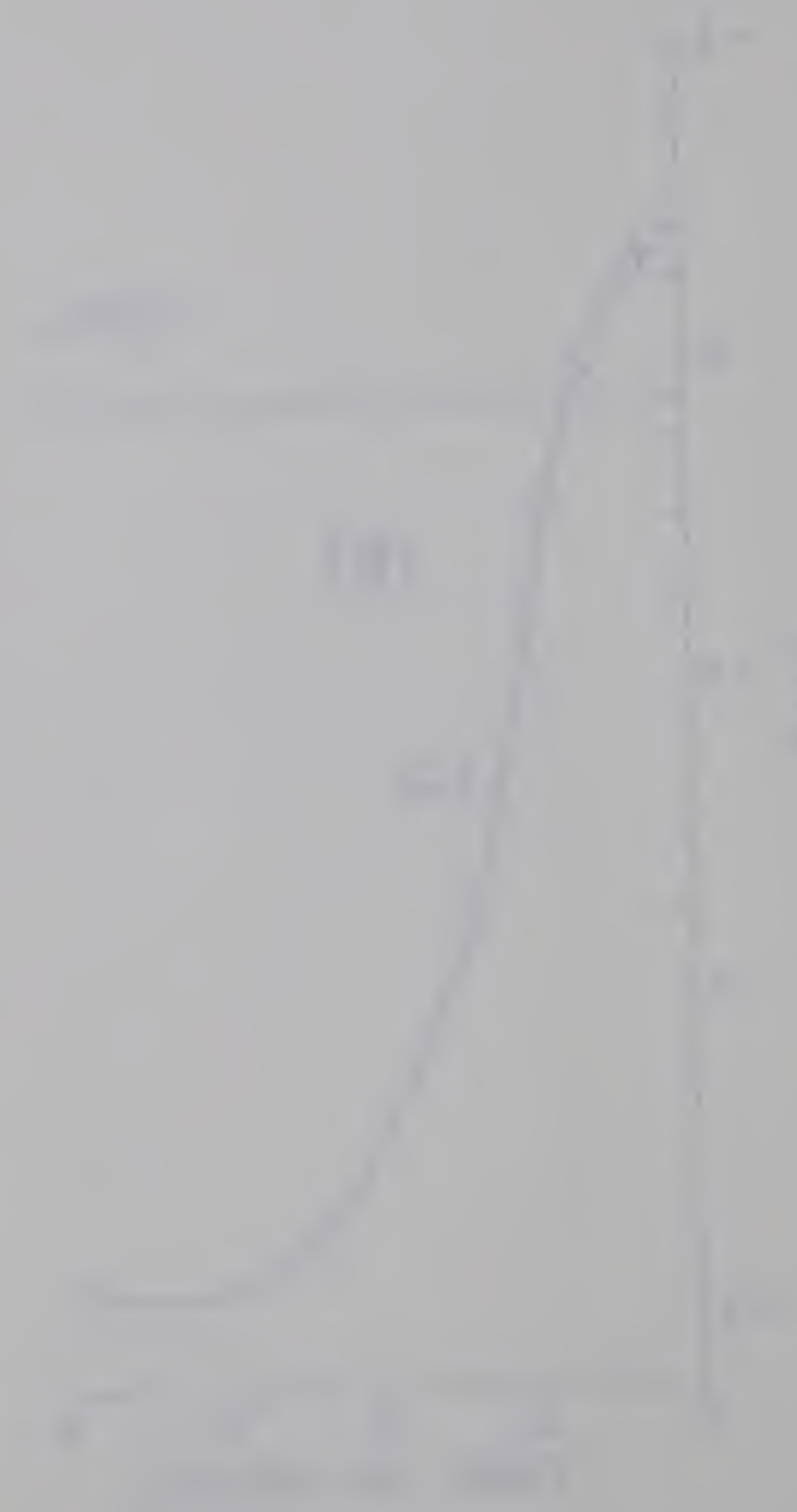
$\delta^{34}S$ of Initial SO_2 = +1.59

Sample	Time of Exchange	$\delta^{34}S$ of SO_2
E-1	20 m	+1.46
E-2	40 m	+1.09
E-3	1 h	+0.26
E-4	1 h - 20 m	-0.14
E-5	1 h - 50 m	-1.83
E-6	2 h - 50 m	-7.04
E-7	4 h - 51 m	-11.16
E-8	7 h - 51 m	-11.74

FIGURES

IX and IX-a: Series (E), Equilibration of H_2SO_4 and SO_2 at 265°C, SO_2 pressure 400 mm Hg.

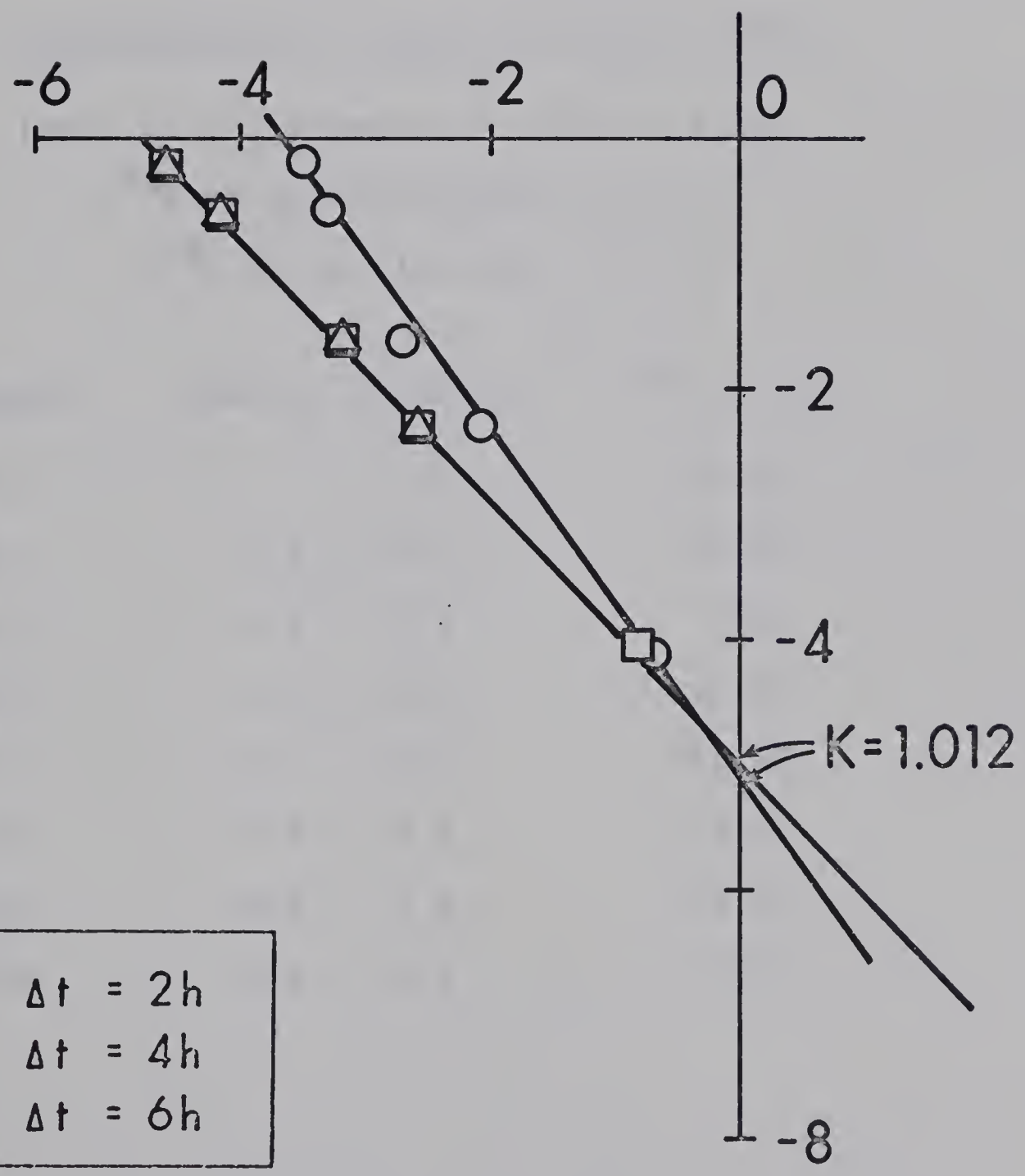

+4
0
-4
-8
-12
$\delta^{34}S$
H_2SO_4
(E)
SO_2
0
2
4
6
8
TIME IN HOURS



1000 ln α_i

1000 ($\ln \alpha_f - \ln \alpha_i$)

(E)



○ Δt = 2h

□ Δt = 4h

△ Δt = 6h



TABLE X

Series P

Equilibration of H_2SO_4 and SO_2 at 254°C

(Initial SO_2 pressure = 300 mm of Hg)

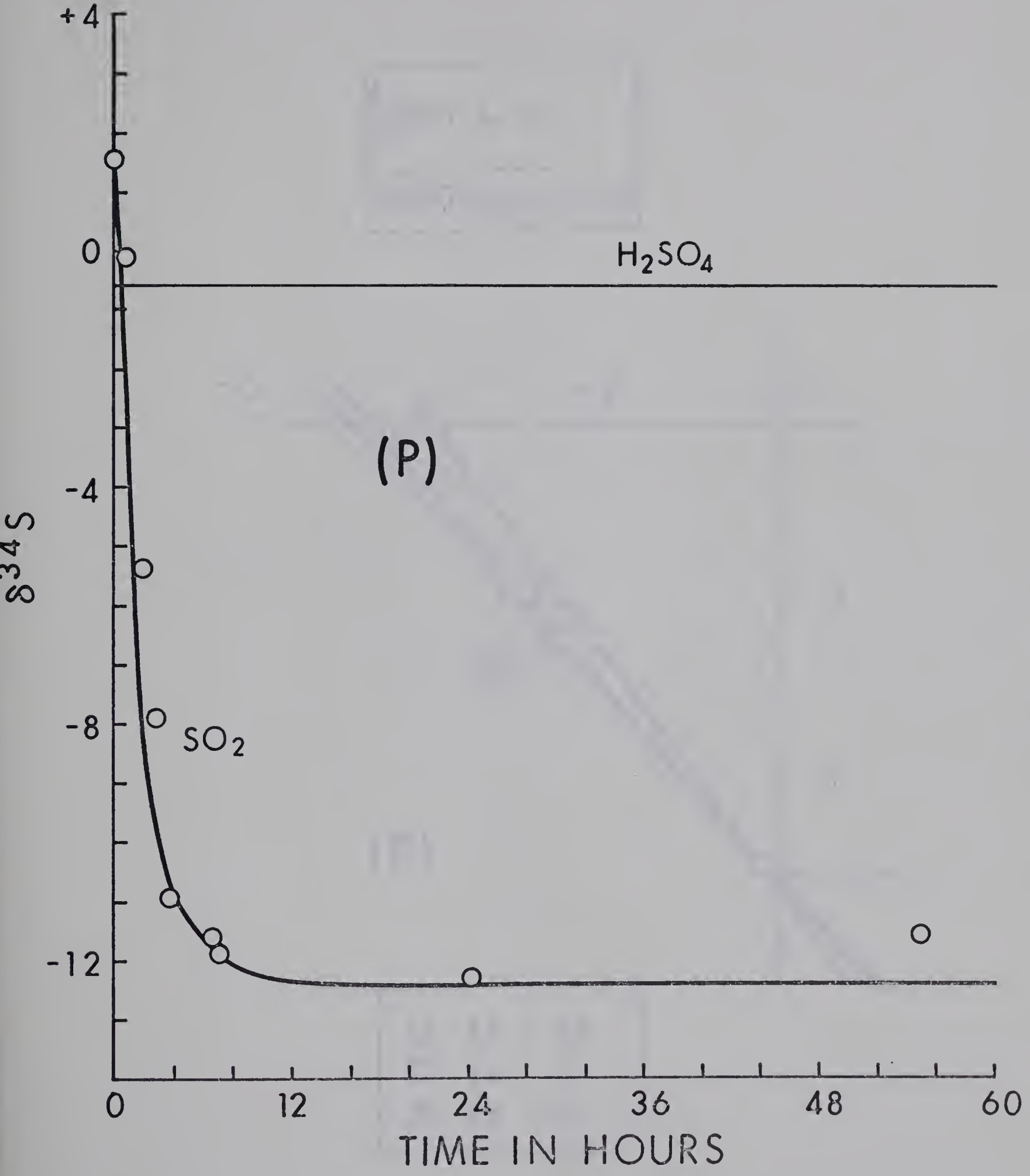
$\delta^{34}S$ of Initial H_2SO_4 = -0.57

$\delta^{34}S$ of Initial SO_2 = +1.59

Sample	Time of Exchange	$\delta^{34}S$ of SO_2
P-1	52 m	-0.13
P-2	1 h - 53 m	-5.37
P-3	2 h - 35 m	-7.91
P-4	3 h - 52 m	-10.90
P-5	6 h - 37 m	-11.59
P-6	7 h - 15 m	-11.90
P-7	24 h - 5 m	-12.30
P-8	54 h - 50 m	-11.57

FIGURES

X and X-a: Series (P), Equilibration of H_2SO_4 and SO_2 at 254°C, SO_2 pressure 100 mm Hg.


+4
0
-4
-8
-12
$\delta^{34}S$
H_2SO_4
(P)
SO_2
0
12
24
36
48
60
TIME IN HOURS



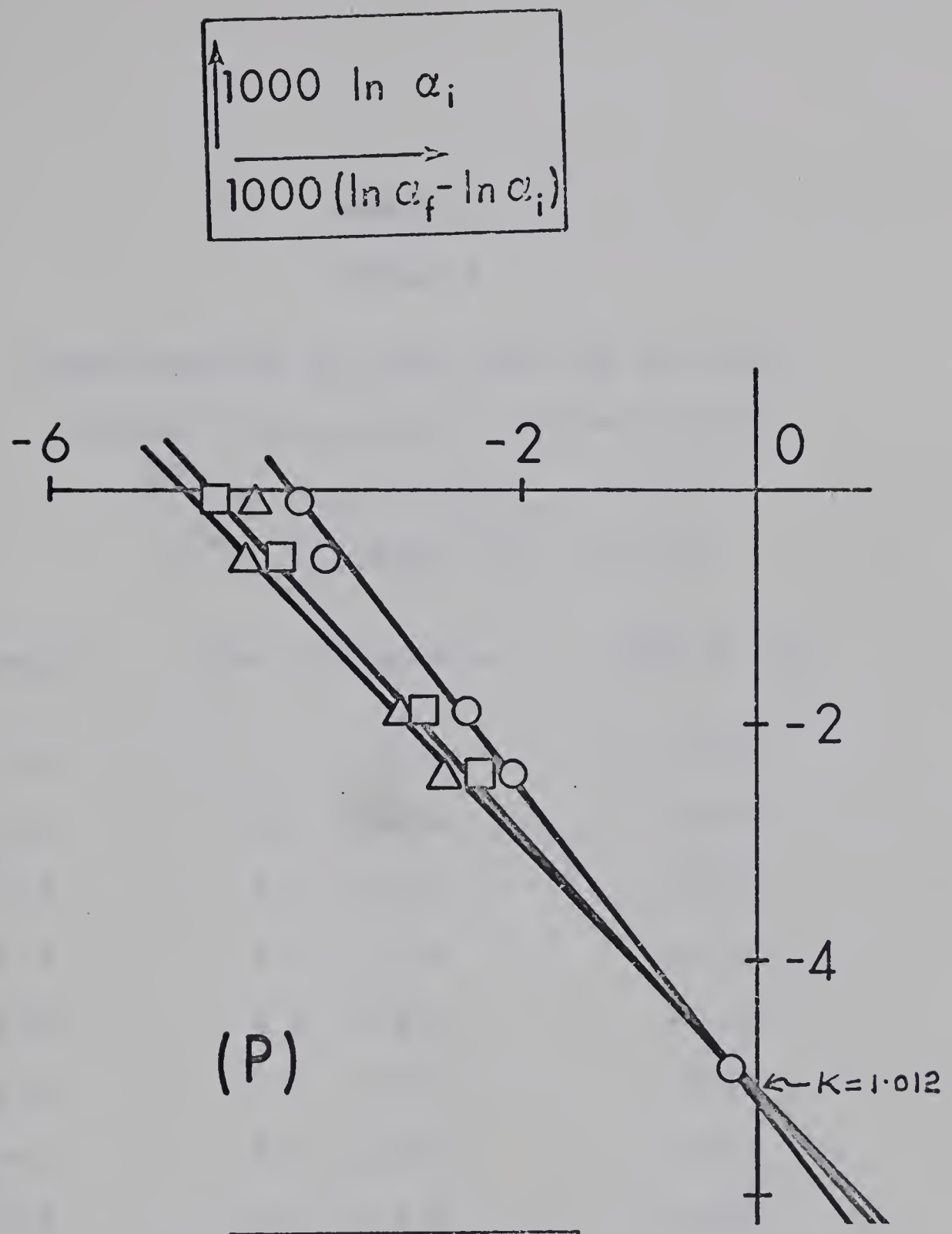

1000 ln α_i
1000 (ln α_f - ln α_i)
-6
-2
0
-2
-4
K=1·012
(P)
○ Δt = 2h
□ Δt = 4h
△ Δt = 6h

TABLE XI

Series F

Equilibration of H_2SO_4 and SO_2 at 240°C

(Initial SO_2 pressure = 10 mm of Hg)

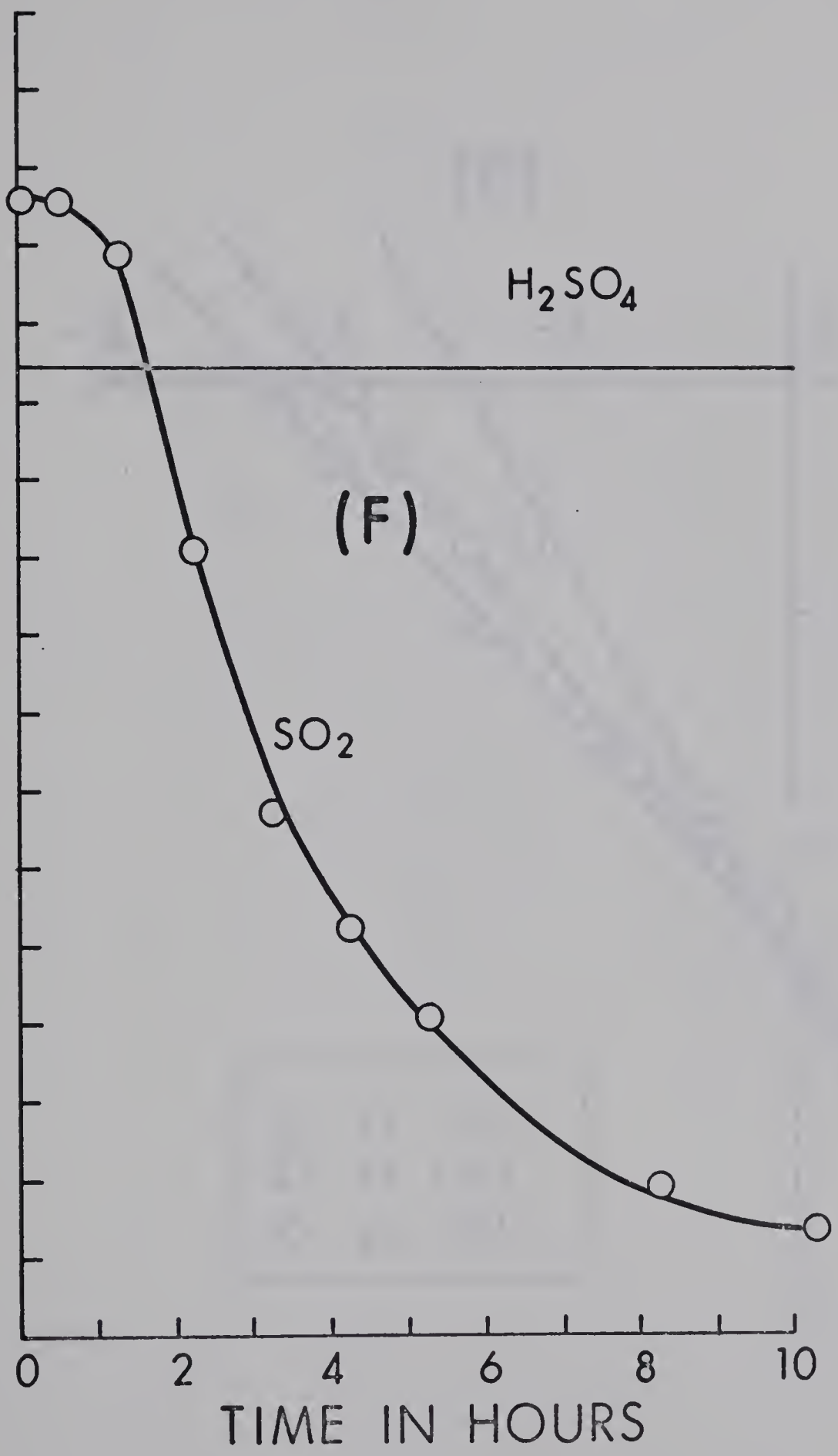
$\delta^{34}S$ of Initial H_2SO_4 = -0.57

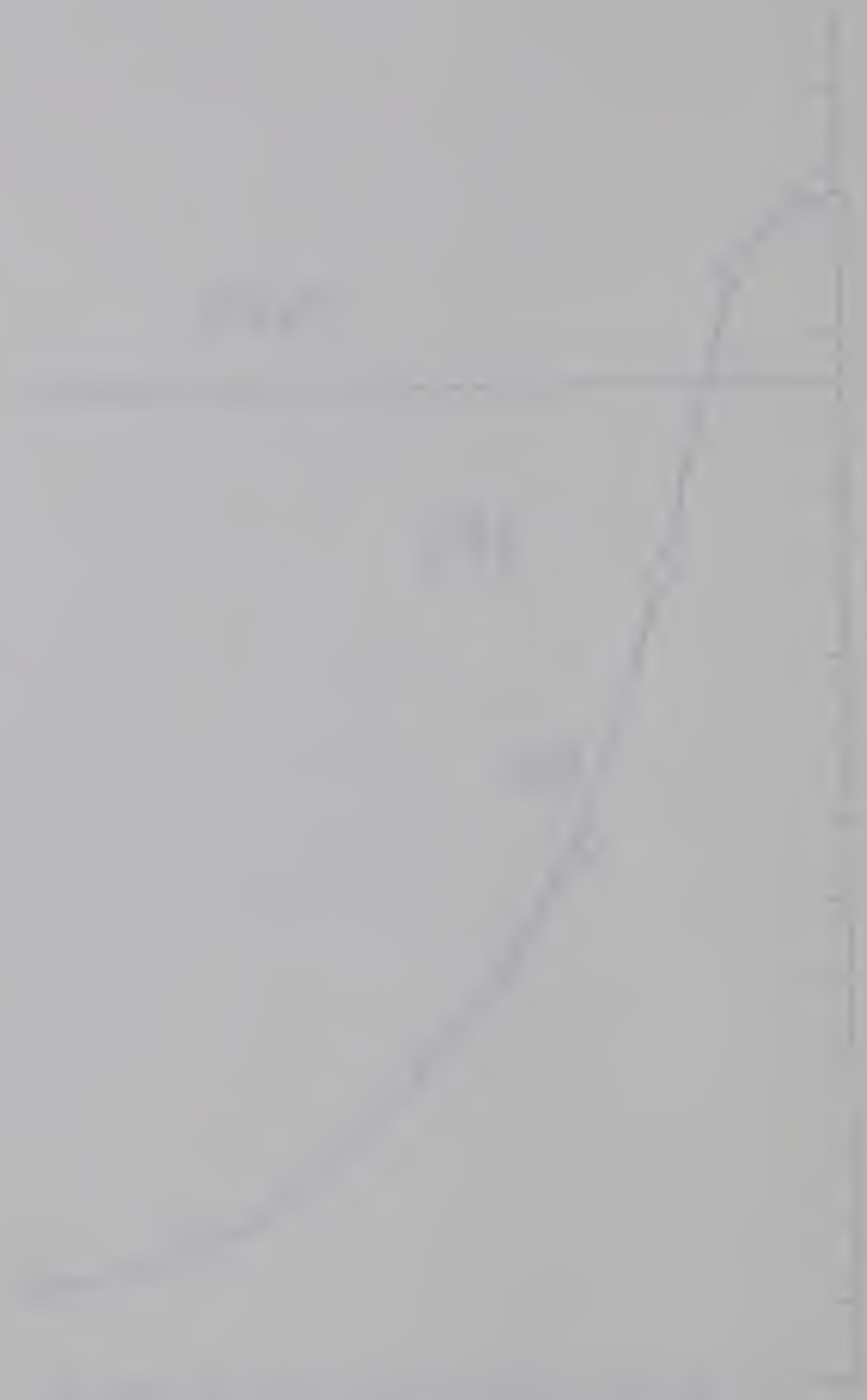
$\delta^{34}S$ of Initial SO_2 = +1.59

Sample	Time of Exchange	$\delta^{34}S$ of SO_2
F-1	30 m	+1.53
F-2	1 h - 15 m	+0.83
F-3	2 h - 15 m	-2.95
F-4	3 h - 15 m	-5.30
F-5	4 h - 15 m	-7.79
F-6	5 h - 15 m	-8.87
F-7	8 h - 15 m	-11.10
F-8	10 h - 15 m	-11.66

FIGURES

XI and XI-a: Series (F), Equilibration of H_2SO_4 and SO_2 at 240°C, SO_2 pressure 10 mm Hg.


H_2SO_4
(F)
SO_2
0
2
4
6
8
10
TIME IN HOURS



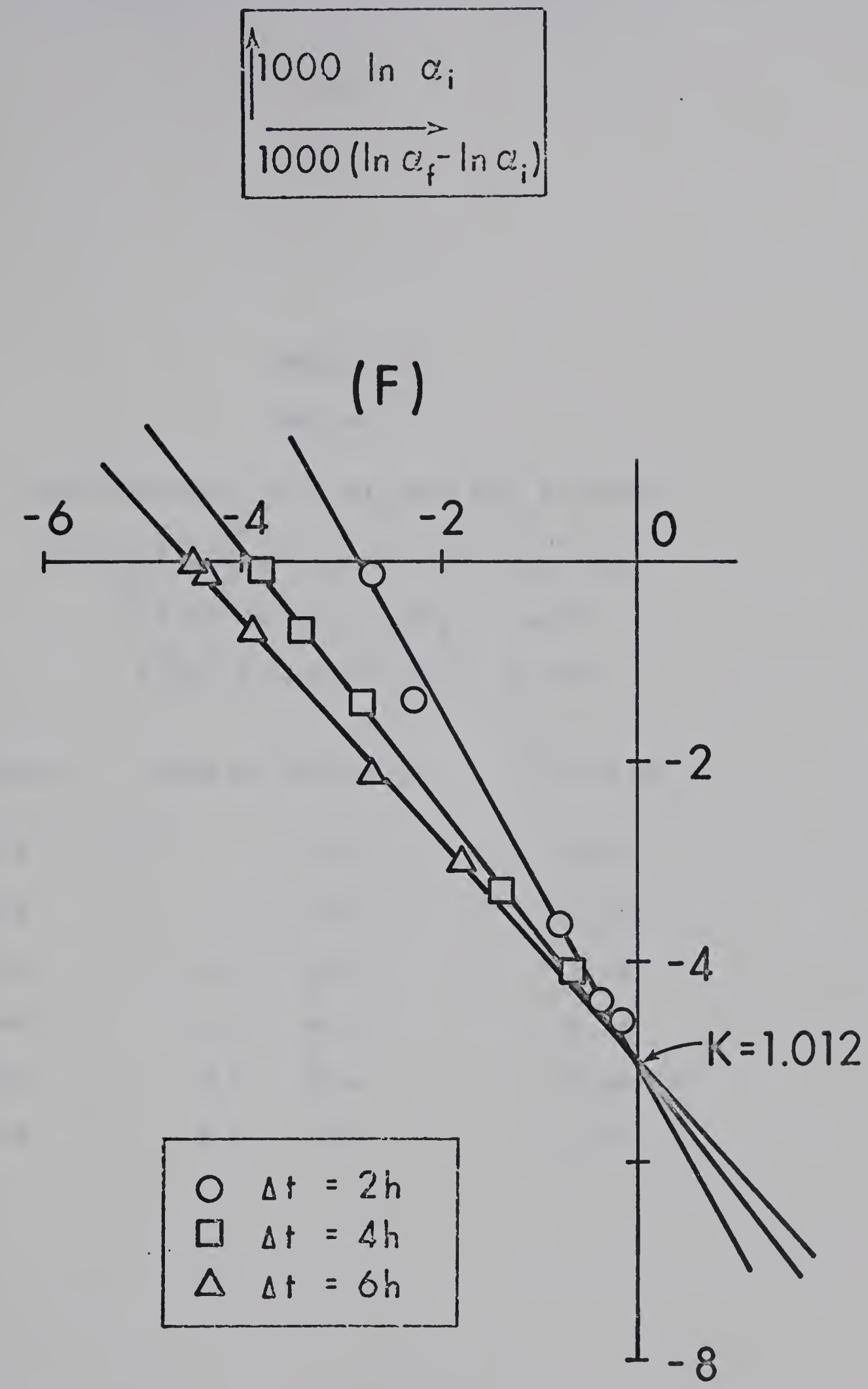

1000 ln α_i
1000 (ln α_f - ln α_i)
(F)
-6
-4
-2
0
-2
-4
K=1.012
-8
○ Δt = 2h
□ Δt = 4h
△ Δt = 6h



TABLE XII

Series G

Equilibration of H_2SO_4 and SO_2 at 240°C

(Initial SO_2 pressure = 100 mm of Hg)

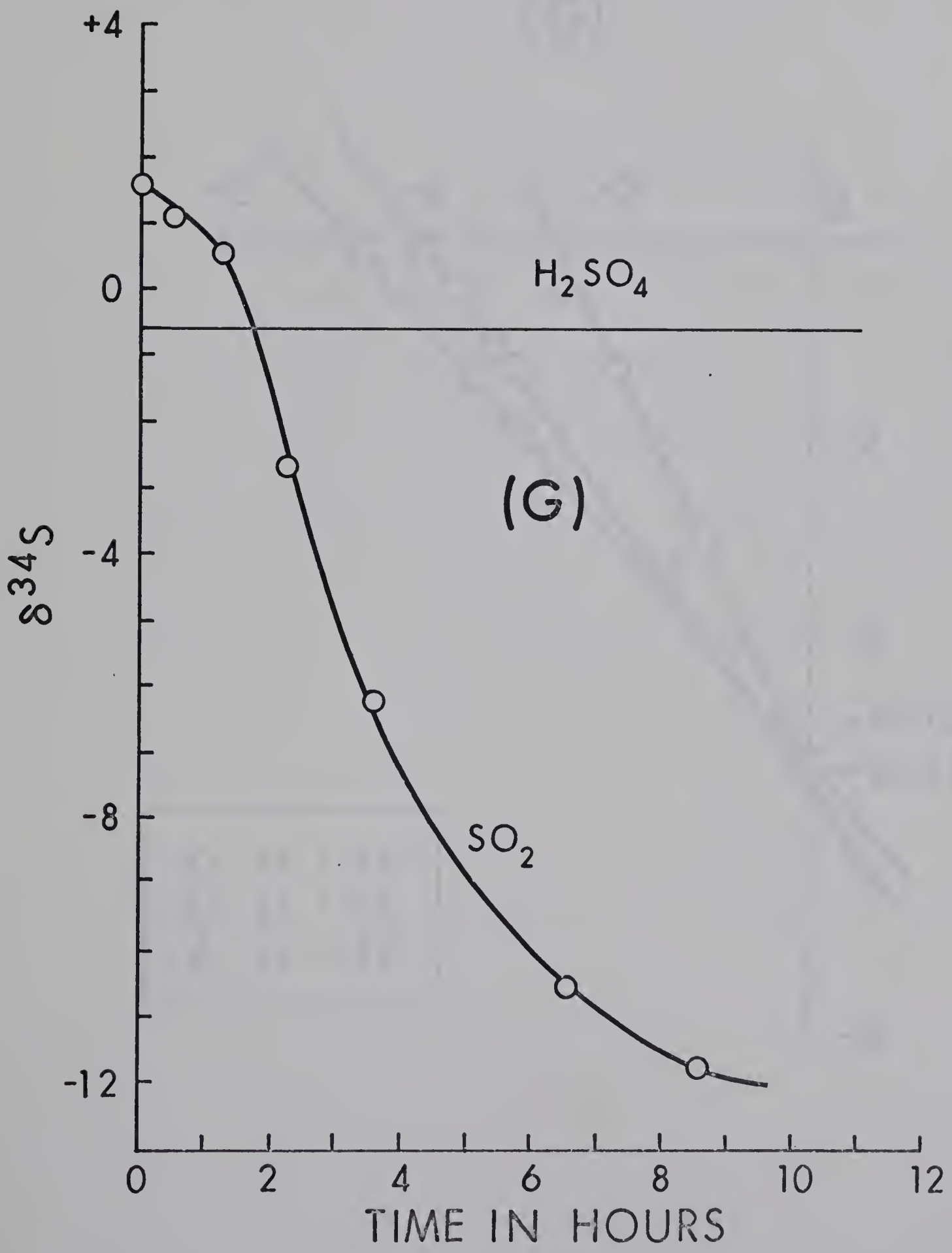
$\delta^{34}S$ of Initial H_2SO_4 = -0.57

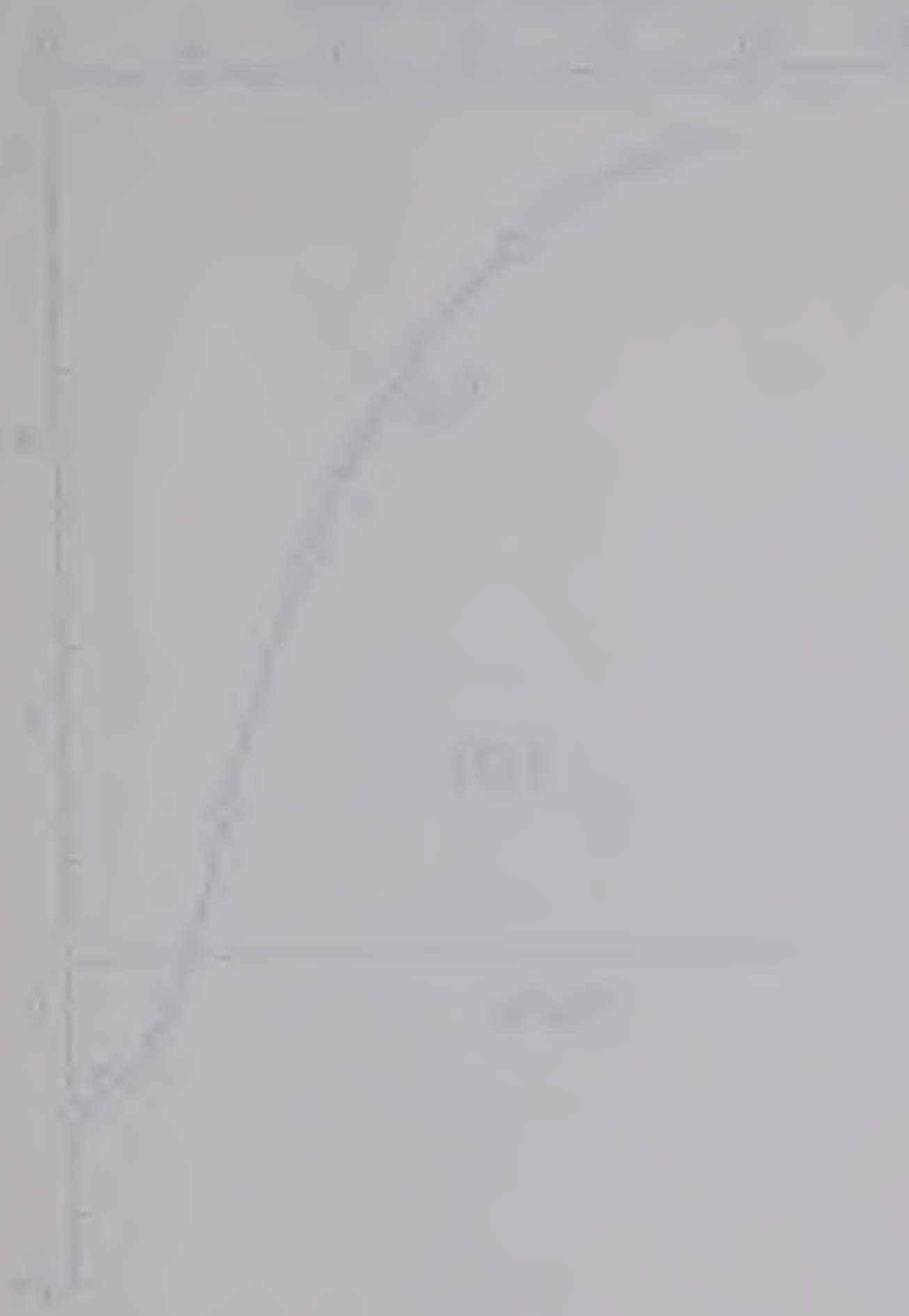
$\delta^{34}S$ of Initial SO_2 = +1.59

Sample	Time of Exchange	$\delta^{34}S$ of SO_2
G-1	30 m	+1.07
G-2	1 h - 15 m	+0.57
G-3	2 h - 15 m	-2.68
G-4	3 h - 34 m	-6.25
G-5	6 h - 34 m	-10.56
G-6	8 h - 34 m	-11.79

FIGURES

XII and XII-a: Series (G), Equilibration of H_2SO_4 and SO_2 at 240°C, SO_2 pressure 100 mm Hg.


+4
0
-4
-8
-12
$\delta^{34}S$
H_2SO_4
(G)
SO_2
0
2
4
6
8
10
12
TIME IN HOURS



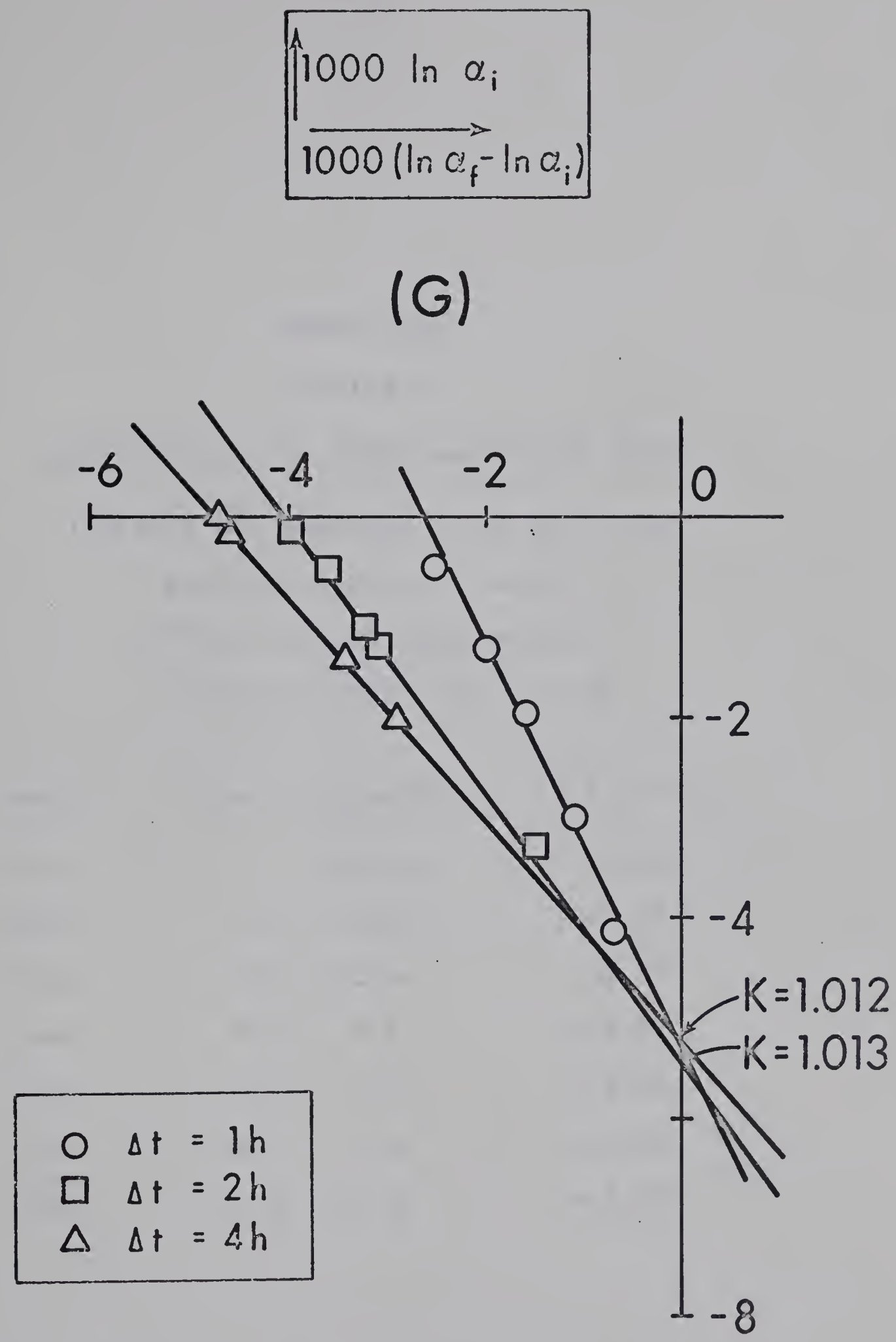

1000 ln α_i
1000 (ln α_f - ln α_i)
(G)
-6
-4
-2
0
-2
-4
-8
K=1.012
K=1.013
Δt = 1h
Δt = 2h
Δt = 4h



TABLE XIII

Series H

Equilibration of H_2SO_4 and SO_2 at 240°C

(Initial SO_2 pressure = 200 mm of Hg)

Air Introduced 200 mm Hg

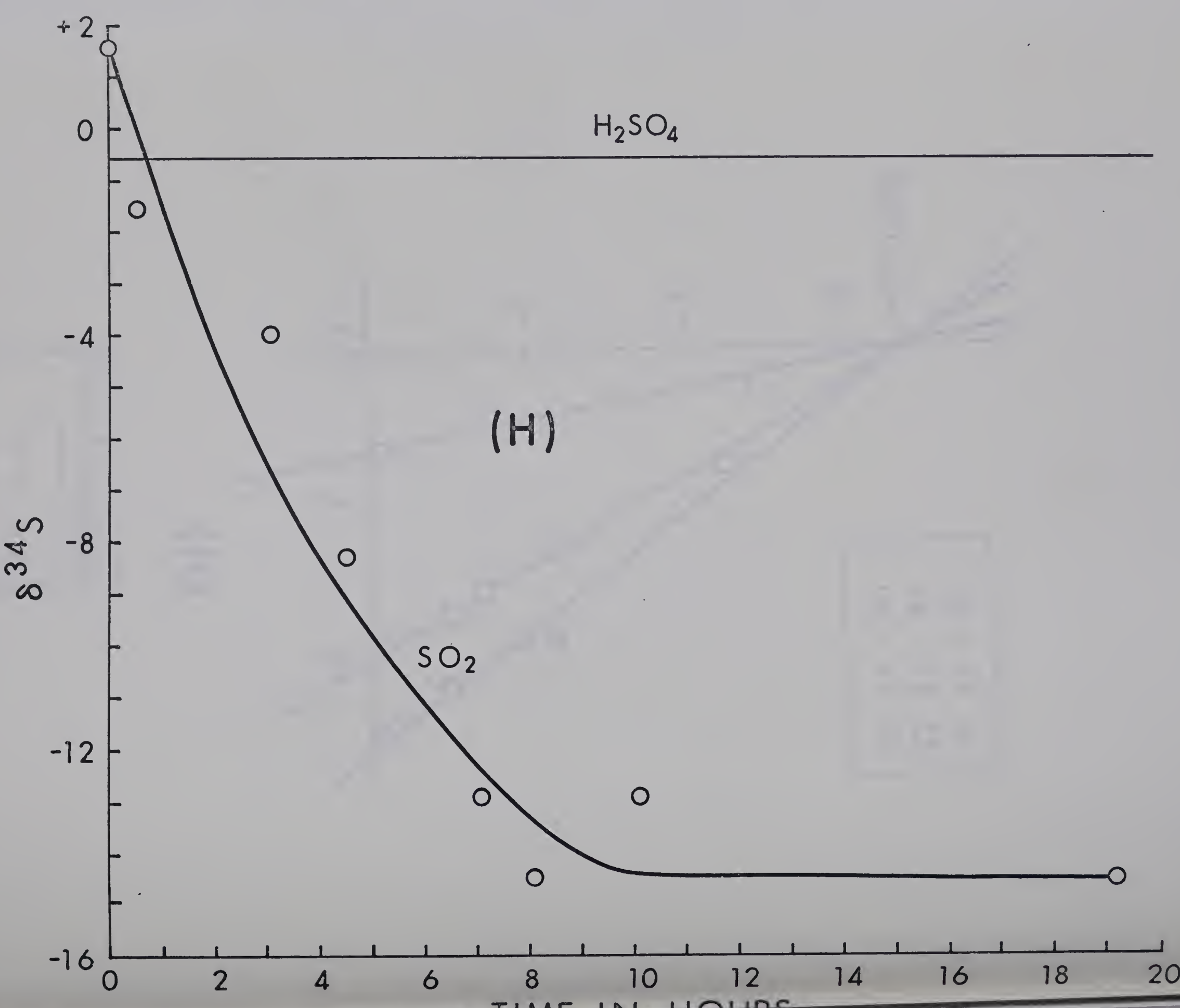
$\delta^{34}S$ of Initial H_2SO_4 = +0.57

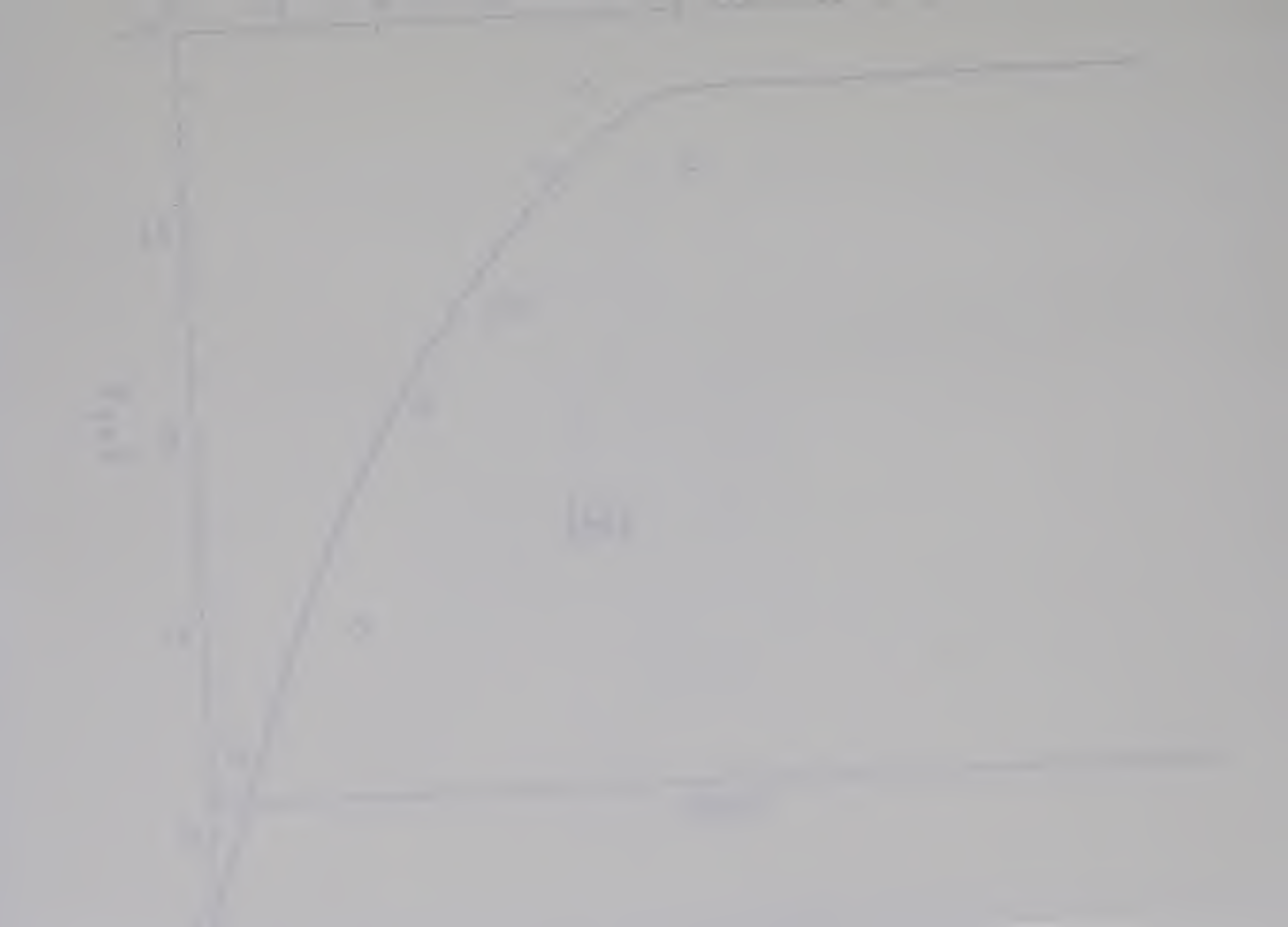
$\delta^{34}S$ of Initial SO_2 = +1.59

Sample	Time of Exchange	$\delta^{34}S$ of SO_2
H-1	32 m	-1.57
H-2	3 h - 2 m	-3.97
H-3	4 h - 32 m	-8.29
H-4	7 h - 2 m	-12.92
H-5	8 h - 2 m	-14.50
H-6	10 h - 3 m	-12.92
H-7	19 h - 12 m	-14.48

FIGURES

XIII and XIII-a: Series (H), Equilibration of H_2SO_4 and SO_2 at 240°C, SO_2 pressure 200 mm Hg. "AIR" introduced, 200 mm Hg.

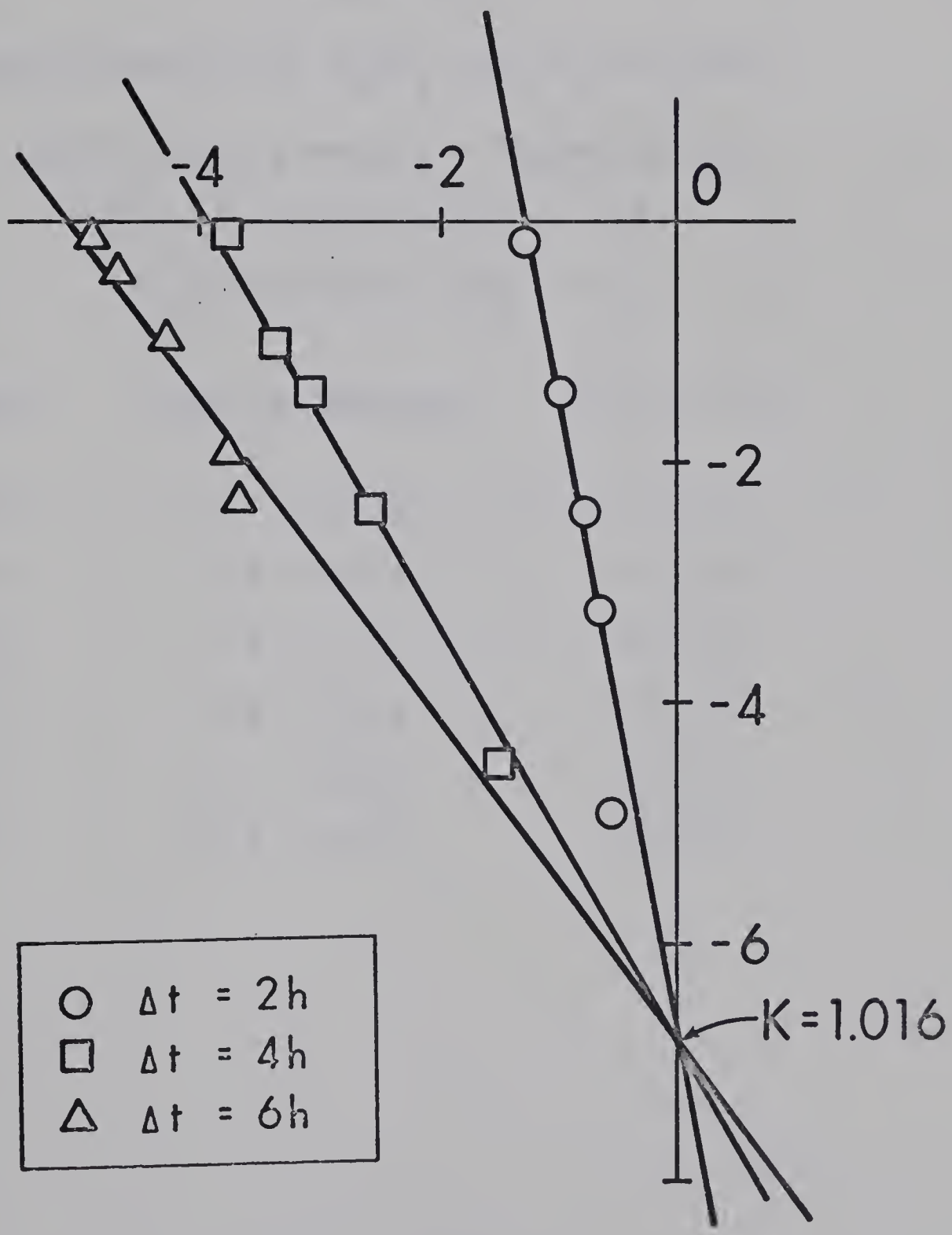

+2
0
-4
-8
-12
-16
$\delta^{34}S$
H_2SO_4
(H)
SO_2
0
2
4
6
8
10
12
14
16
18
20
TIME IN HOURS



1000 ln α_i

1000 (ln α_f - ln α_i)

(H)



○ Δt = 2h
□ Δt = 4h
△ Δt = 6h



TABLE XIV

Series I

Equilibration of H_2SO_4 and SO_2 at 240°C

(Initial SO_2 pressure = 400 mm of Hg)

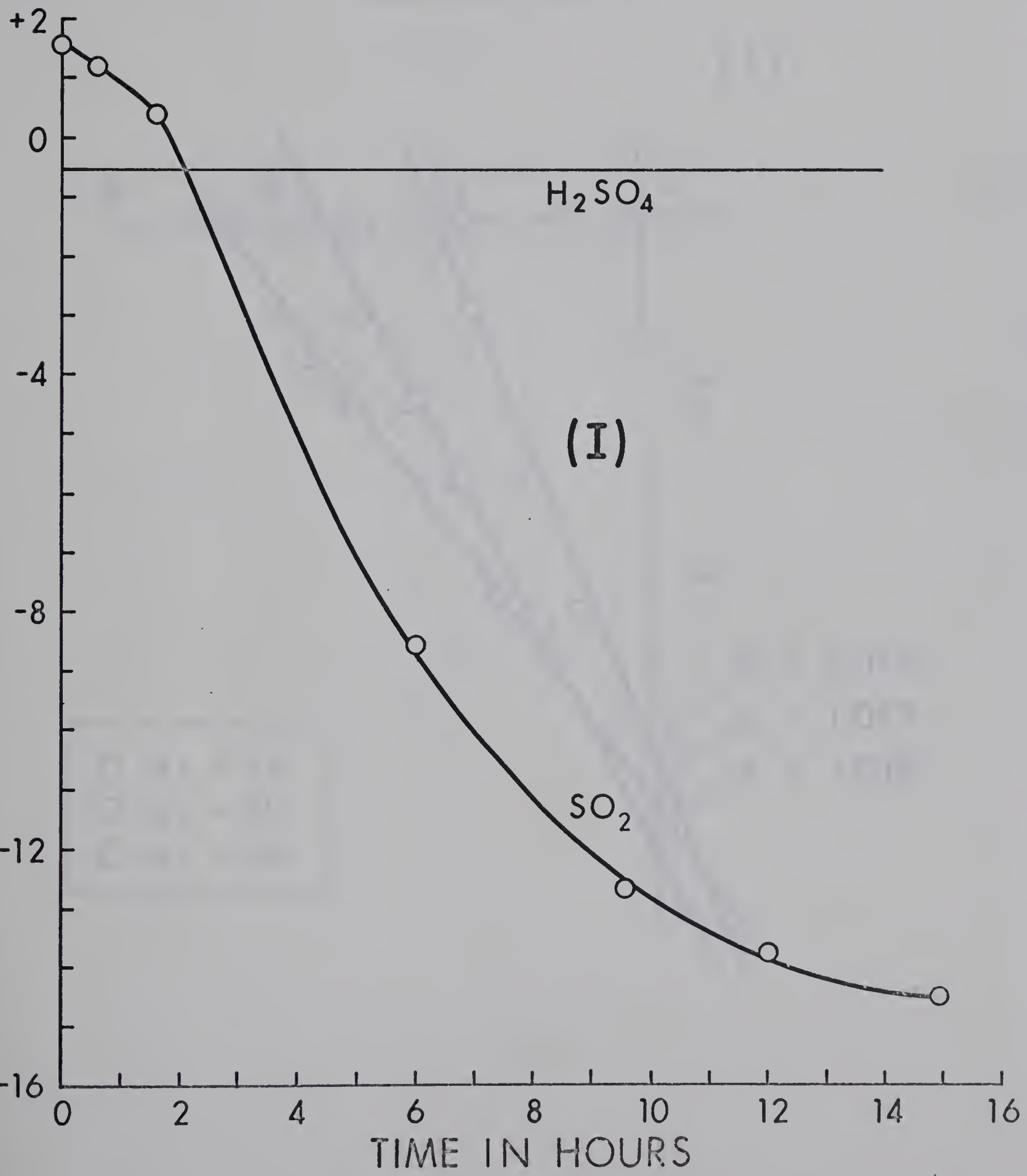
$\delta^{34}S$ of Initial H_2SO_4 = -0.57

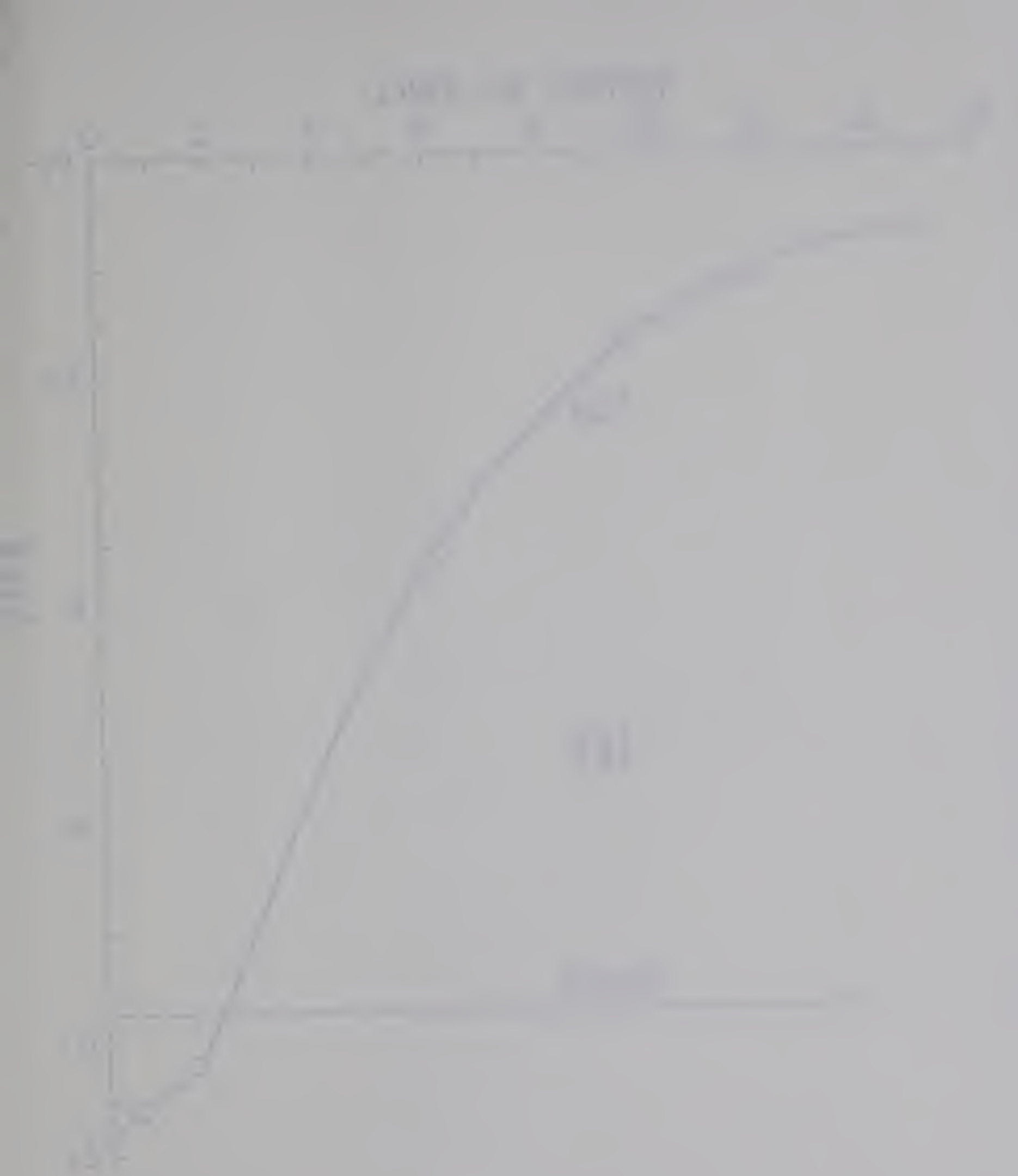
$\delta^{34}S$ of Initial SO_2 = +1.59

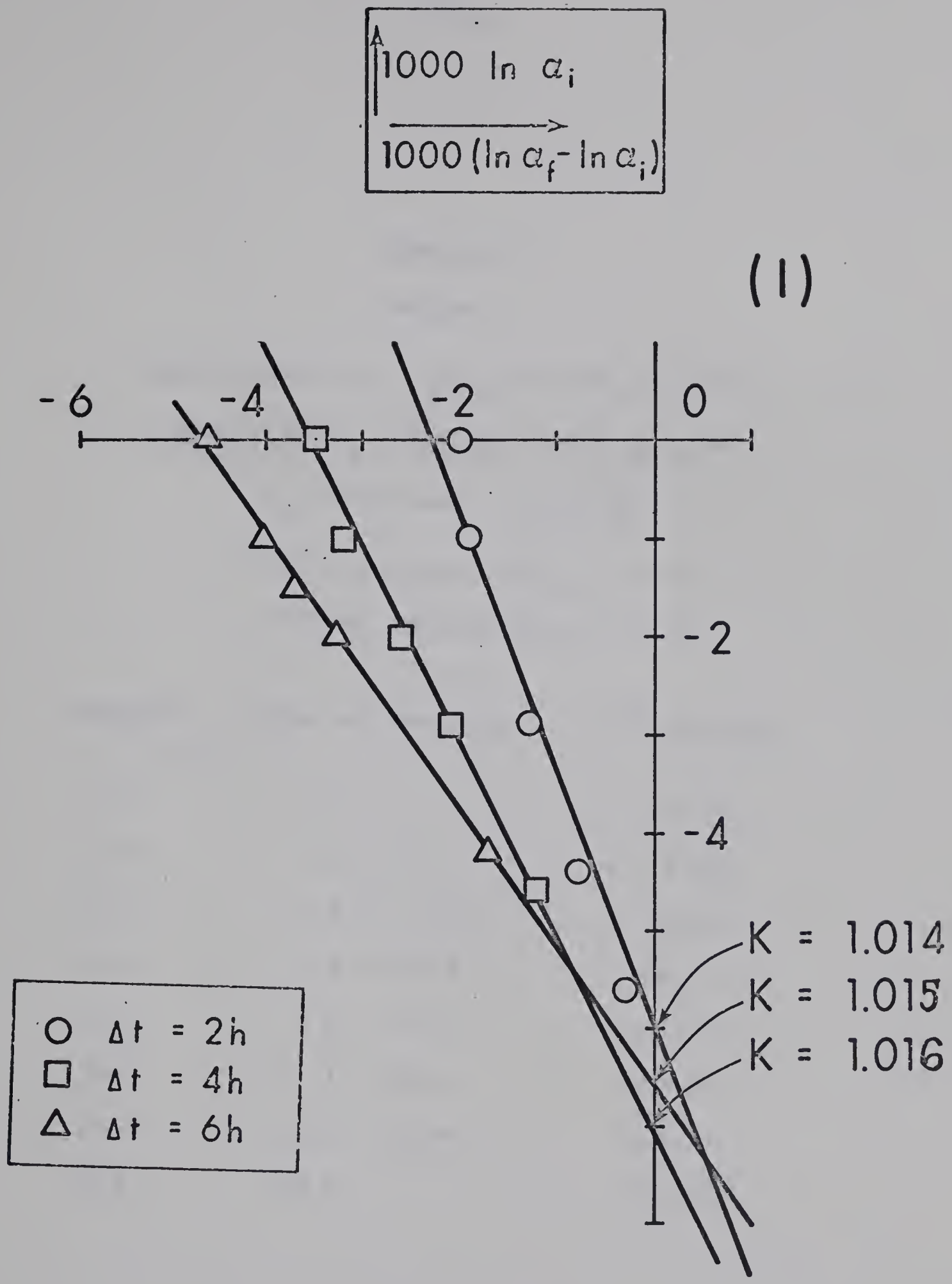
Sample	Time of Exchange	$\delta^{34}S$ of SO_2
I-1	35 m	+1.17
I-2	1 h - 33 m	+0.33
I-3	6 h	-8.54
I-4	9 h - 31 m	-12.70
I-5	11 h - 59 m	-13.77
I-6	14 h - 54 m	-14.52

FIGURES

XIV and XIV-a: Series (I), Equilibration of H_2SO_4 and SO_2 at 240°C, SO_2 pressure 400 mm Hg.


+2
0
-4
-8
-12
-16
δ34S
H2SO4
(I)
SO2
0
2
4
6
8
10
12
14
16
TIME IN HOURS




1000 ln a_i
1000 (ln a_f - ln a_i)
(1)
-6
-4
-2
0
-2
-4
K = 1.014
K = 1.015
K = 1.016
○ Δt = 2h
□ Δt = 4h
△ Δt = 6h

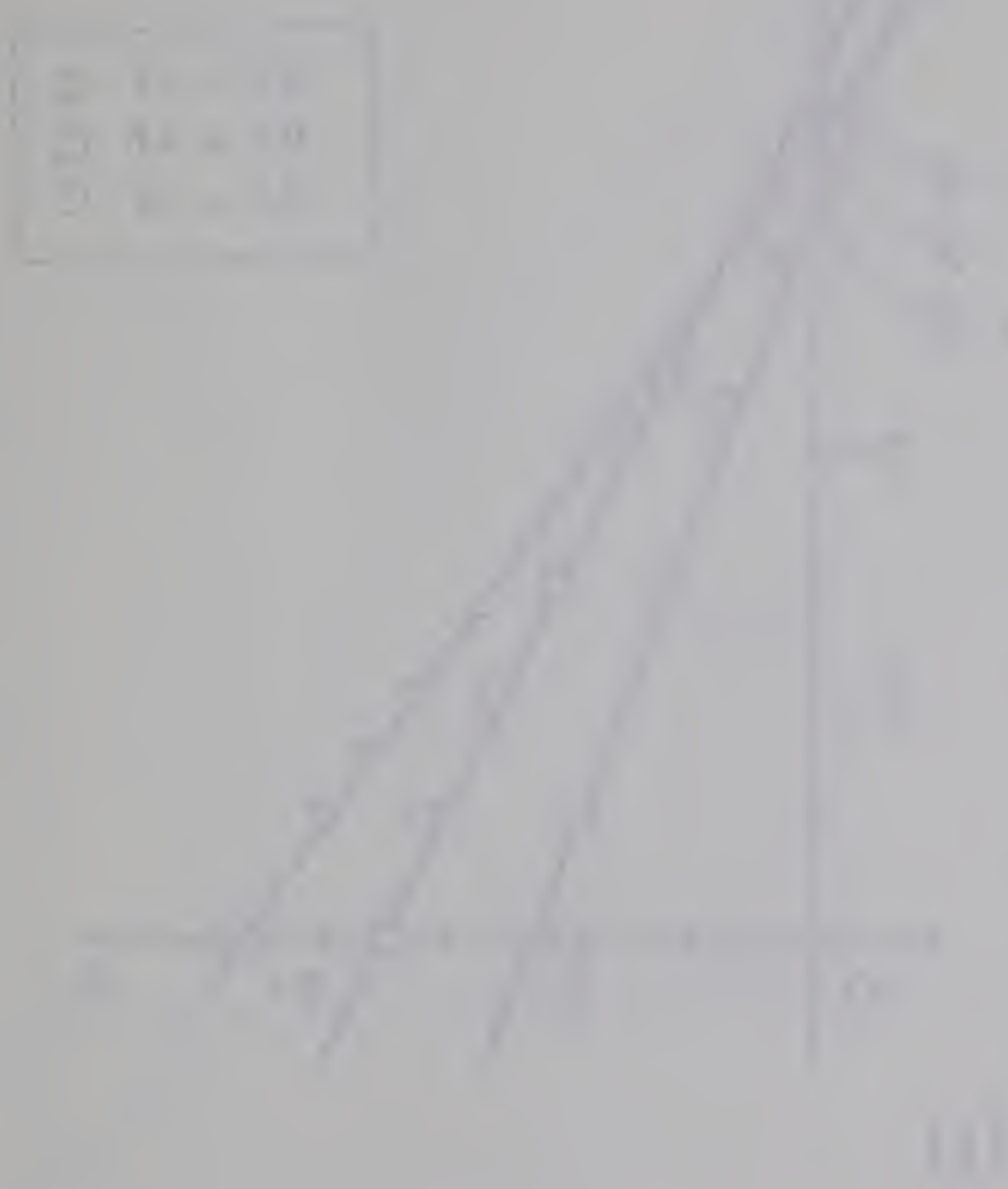


TABLE XV

Series J

Equilibration of H_2SO_4 and SO_2 at 240°C

(Initial SO_2 pressure = 100 mm Hg)

O_2 introduced, 10 mm Hg

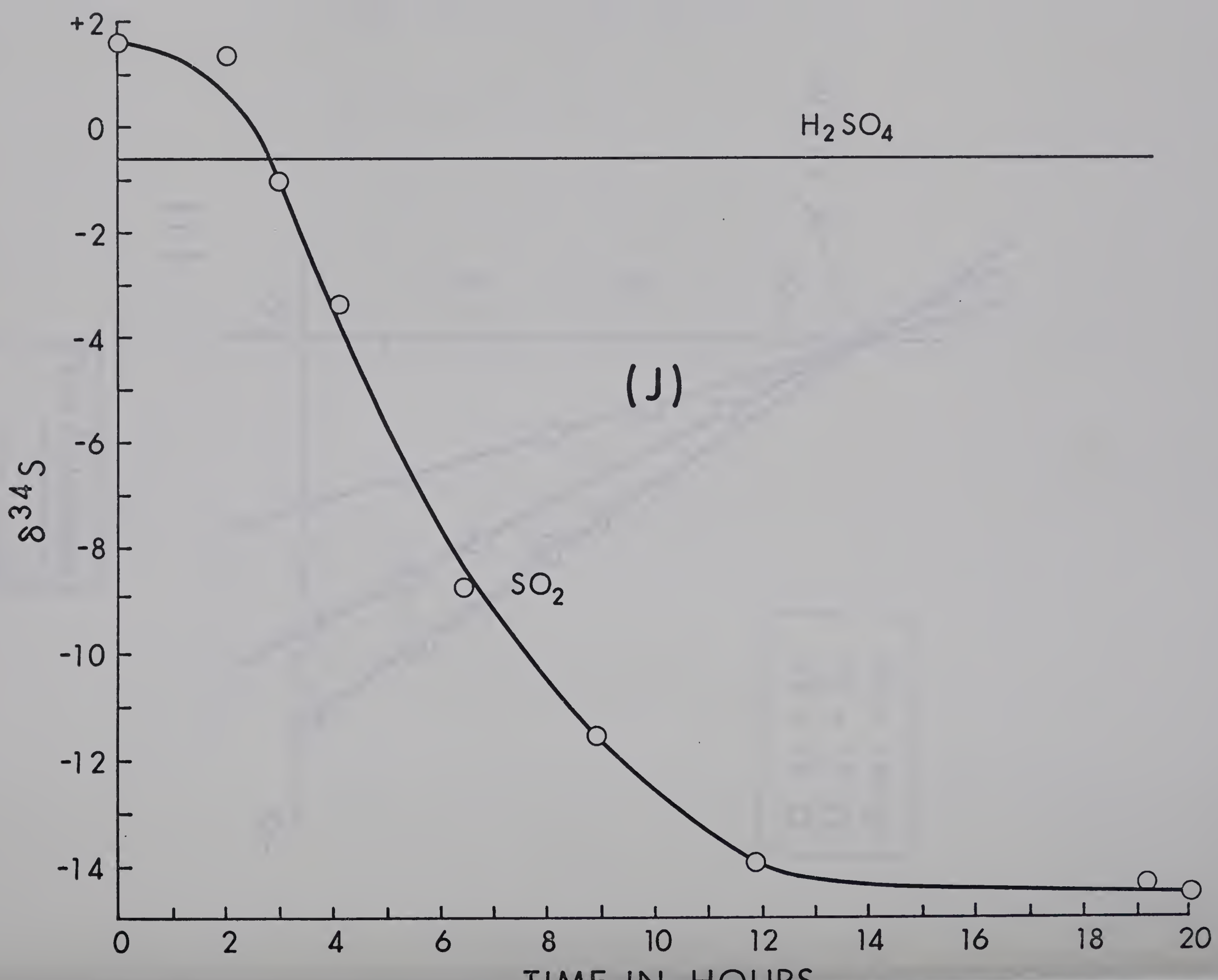
$\delta^{34}S$ of Initial H_2SO_4 = -0.57

$\delta^{34}S$ of Initial SO_2 = +1.59

Sample	Time of Exchange	$\delta^{34}S$ of SO_2
J-1	2 h	+2.34
J-2	3 h	-1.06
J-3	4 h - 7 m	-3.37
J-4	6 h - 29 m	-8.77
J-5	8 h - 57 m	-11.55
J-6	11 h - 53 m	-13.95
J-7	19 h - 10 m	-14.31
J-8	20 h	-14.53

FIGURES

XV and XV-a: Series (J), Equilibration of H_2SO_4 and SO_2 at 240°C, SO_2 pressure 100 mm Hg. "O_2" introduced, 100 mm Hg.


+2
0
-2
-4
-6
-8
-10
-12
-14
$\delta^{34}S$
H_2SO_4
(J)
SO_2
0
2
4
6
8
10
12
14
16
18
20
TIME IN HOURS



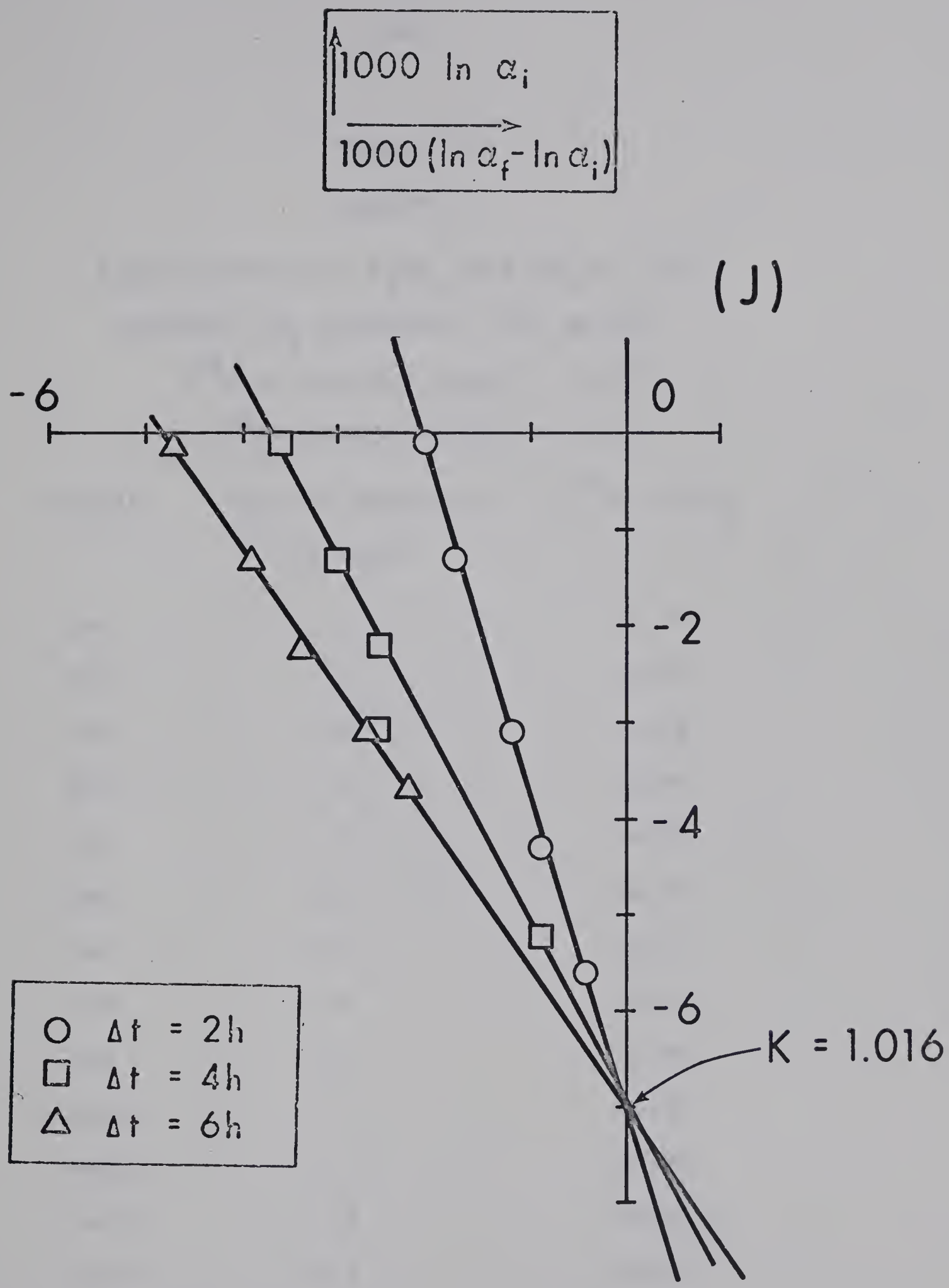

1000 ln α_i
1000 (ln α_f - ln α_i)
(J)
-6
0
-2
-4
-6
K = 1.016
○ Δt = 2h
□ Δt = 4h
△ Δt = 6h



TABLE XVI

Series O

Equilibration of H_2SO_4 and SO_2 at 150°C

(Initial SO_2 pressure = 350 mm Hg)

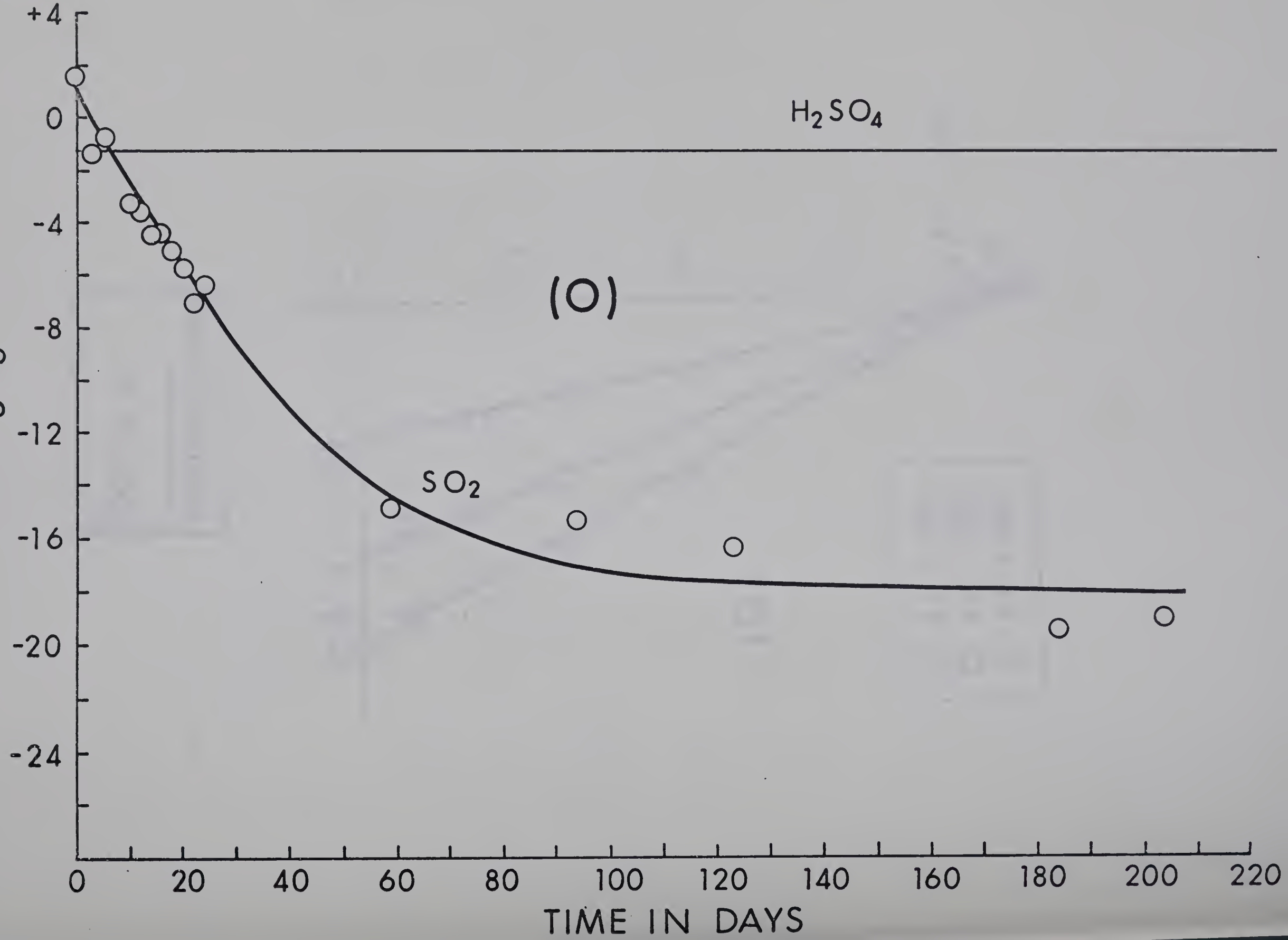
$\delta^{34}S$ of Initial H_2SO_4 = -0.57

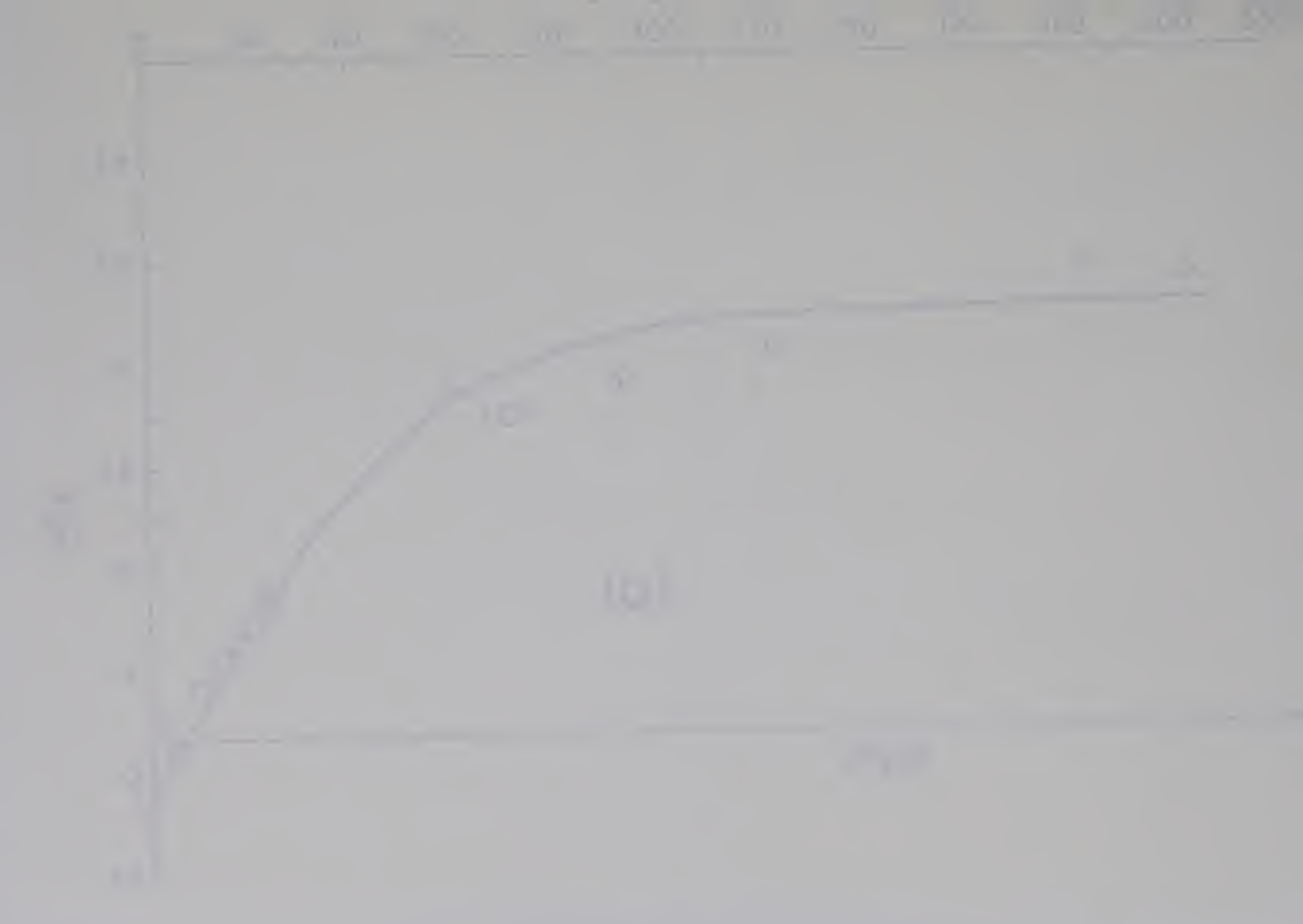
$\delta^{34}S$ of Initial SO_2 = +1.59

Sample	Time of Exchange in Days	$\delta^{34}S$ of SO_2
O-1	3	-1.40
O-2	5	-0.75
O-3	10	-3.24
O-4	12	-3.59
O-5	14	-4.50
O-6	16	-4.49
O-7	18	-5.21
O-8	20	-5.91
O-9	22	-7.04
O-10	24	-6.38
O-11	59	-14.88
O-12	94	-15.37
O-13	123	-16.25
O-14	184	-19.42
O-15	204	-19.05

FIGURES

XVI and XVI-a: Series (O), Equilibration of H_2SO_4 and SO_2 at 150°C, SO_2 pressure 350 mm Hg.


+4
0
-4
-8
-12
-16
-20
-24
$\delta^{34}S$
H_2SO_4
(O)
SO_2
0
20
40
60
80
100
120
140
160
180
200
220
TIME IN DAYS



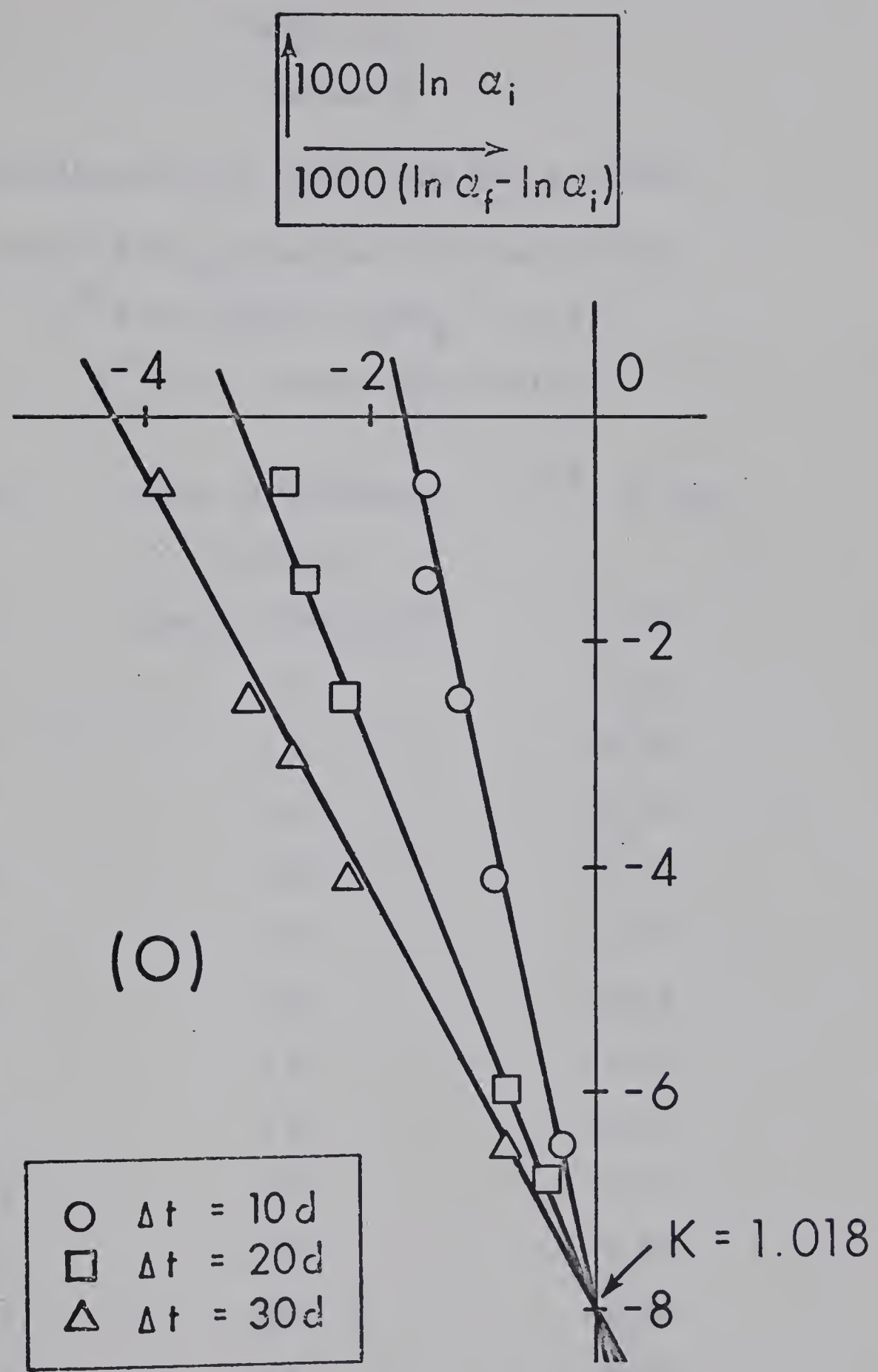

1000 ln α_i
1000 (ln α_f - ln α_i)
-4
-2
0
-2
-4
-6
-8
K = 1.018
(O)
○ Δt = 10 d
□ Δt = 20 d
△ Δt = 30 d



TABLE XVII

Series V

Equilibration of H_2SO_4 and SO_2 at 100°C

(Initial SO_2 pressure = 300 mm of Hg)

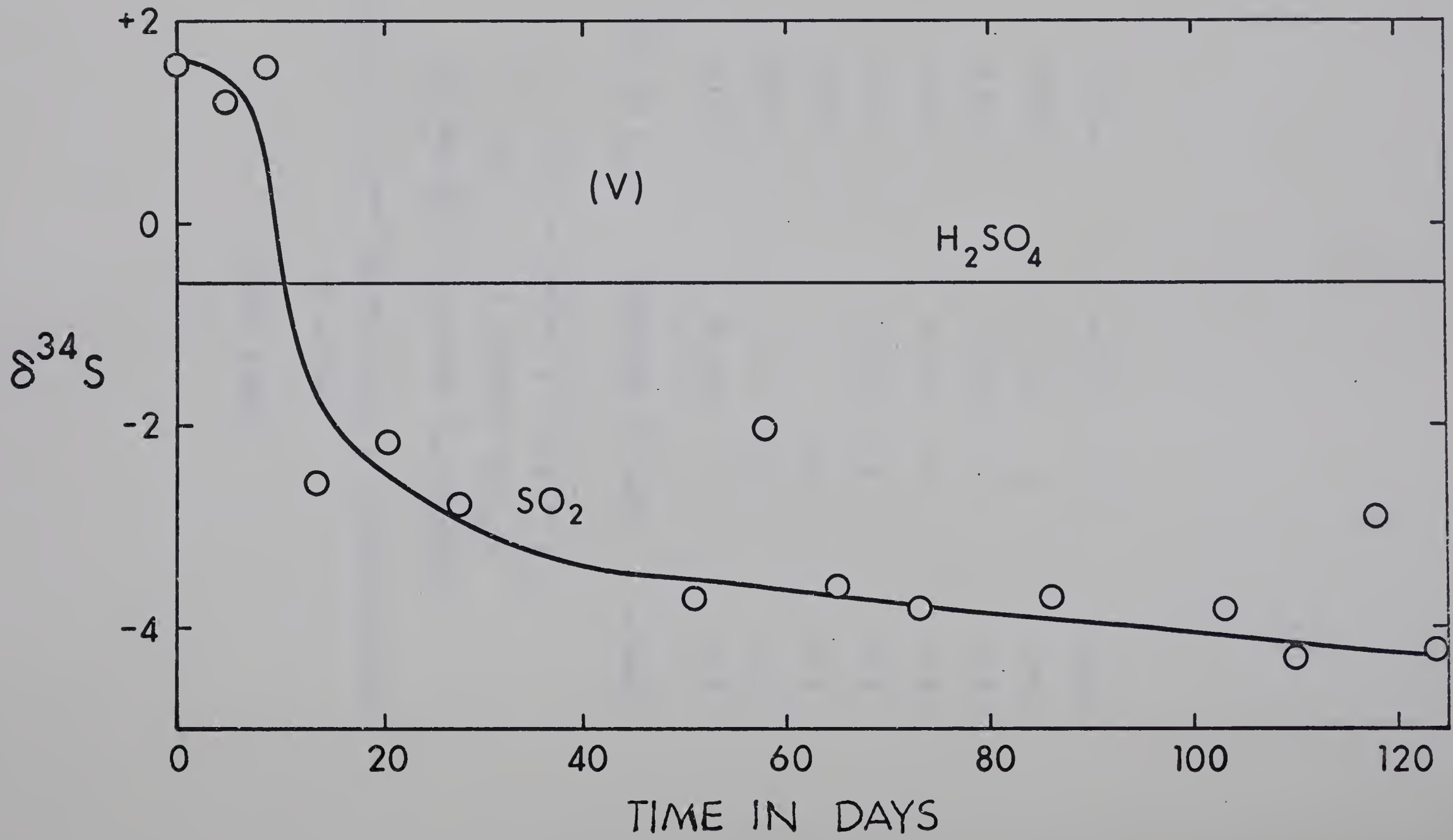
$\delta^{34}S$ of Initial H_2SO_4 = -0.57

$\delta^{34}S$ of Initial SO_2 = +1.59

Sample	Time of Exchange in Days	$\delta^{34}S$ of SO_2
V-1	Start 5 Feb. 1966	+1.22
V-2	9	+1.58
V-3	14	-2.56
V-4	21	-2.15
V-5	28	-2.78
V-6	51	-3.72
V-7	58	-2.01
V-8	65	-3.56
V-9	73	-3.81
V-10	86	-3.71
V-11	103	-3.82
V-12	110	-4.30
V-13	118	-2.92
V-14	124	-4.23

FIGURES

XVII and XVII-a: Series (V), Equilibration of H_2SO_4 and SO_2 at 100°C, SO_2 pressure 300 mm Hg.


+2
0
-2
-4
$\delta^{34}S$
(V)
H_2SO_4
SO_2
0
20
40
60
80
100
120
TIME IN DAYS

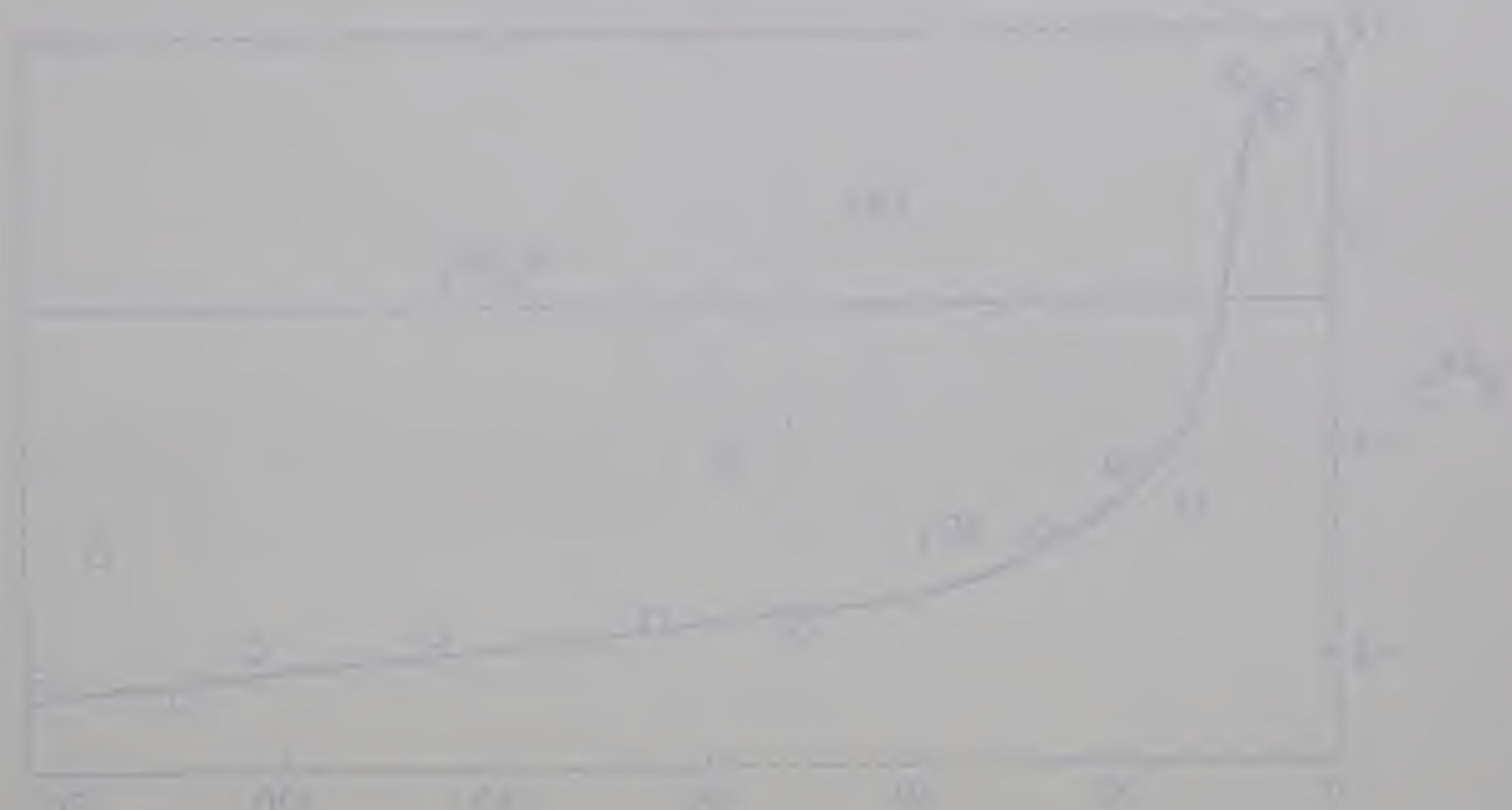


TABLE XVIII

Series K

Equilibration of Solid Na_2SO_4 and SO_2 at 240°C

(Initial SO_2 pressure = 200 mm Hg)

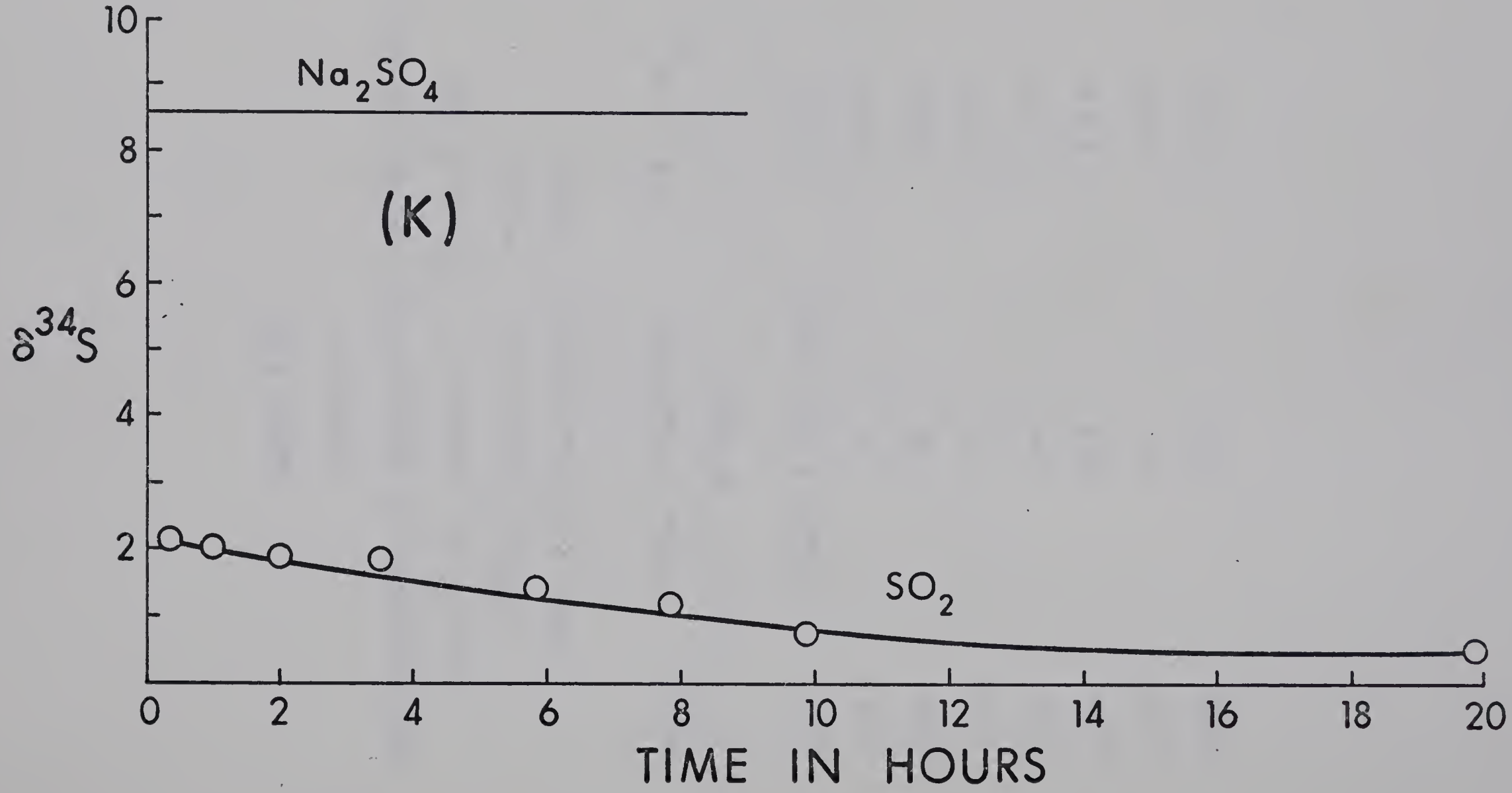
$\delta^{34}S$ of Initial SO_2 = +1.59

$\delta^{34}S$ of Initial Na_2SO_4 = +8.56

Sample	Time of Exchange	$\delta^{34}S$ of SO_2
K-1	20 m	+2.14
K-2	1 h	+2.06
K-3	2 h	+1.89
K-4	3 h - 30 m	+1.85
K-5	5 h - 50 m	+1.41
K-6	7 h - 50 m	+1.19
K-7	9 h - 50 m	+0.81
K-8	19 h - 50 m	+0.50

FIGURE

XVIII: Series (K), Equilibration of Solid Na_2SO_4 and SO_2 at 240°C, SO_2 pressure 200 mm Hg.


10
8
6
4
2
$\delta^{34}S$
Na_2SO_4
(K)
SO_2
0
2
4
6
8
10
12
14
16
18
20
TIME IN HOURS

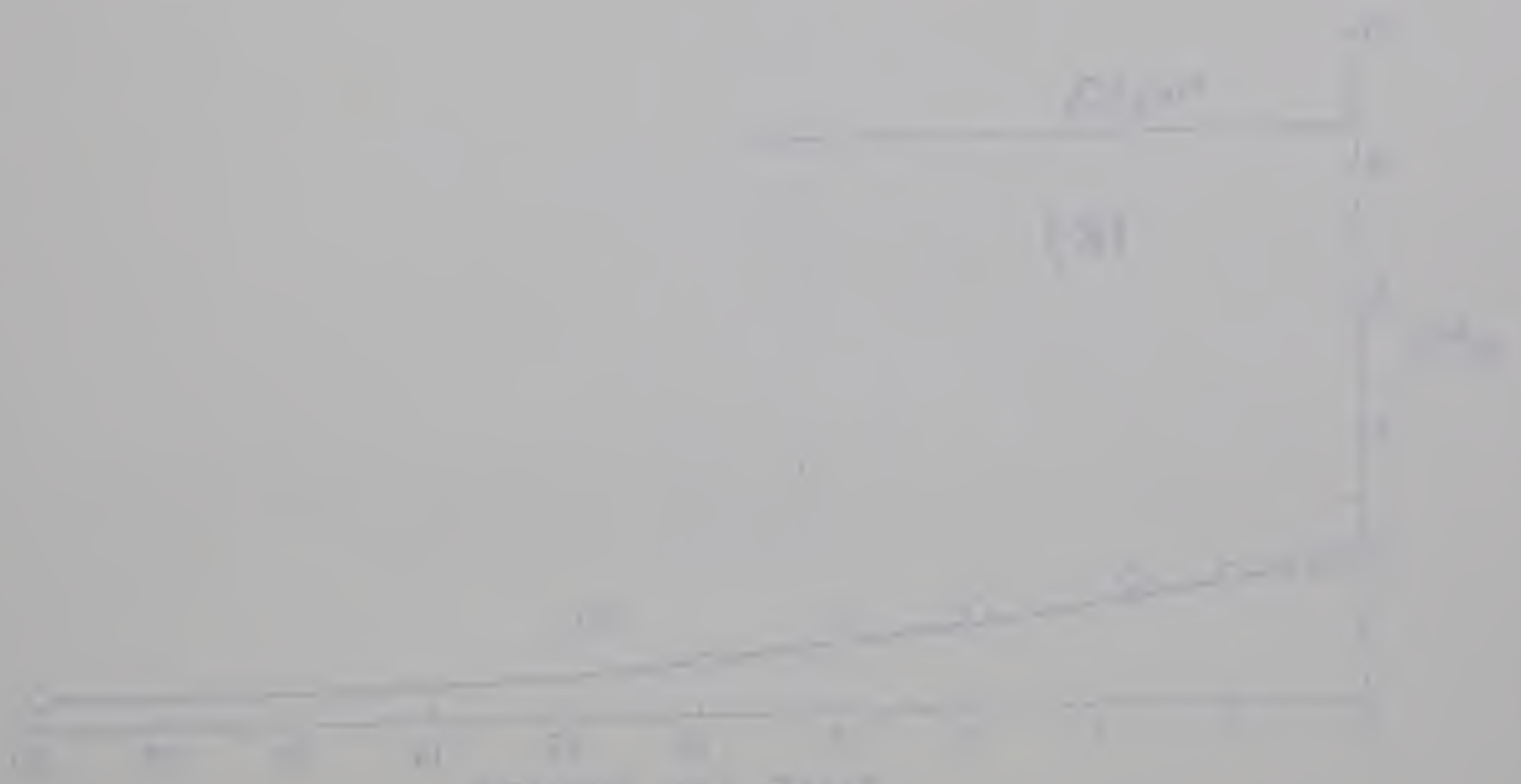


TABLE XIX

Series Q

Equilibration of Na_2SO_4(soln) and SO_2 at 100°C

(Initial SO_2 pressure = 200 mm of Hg)

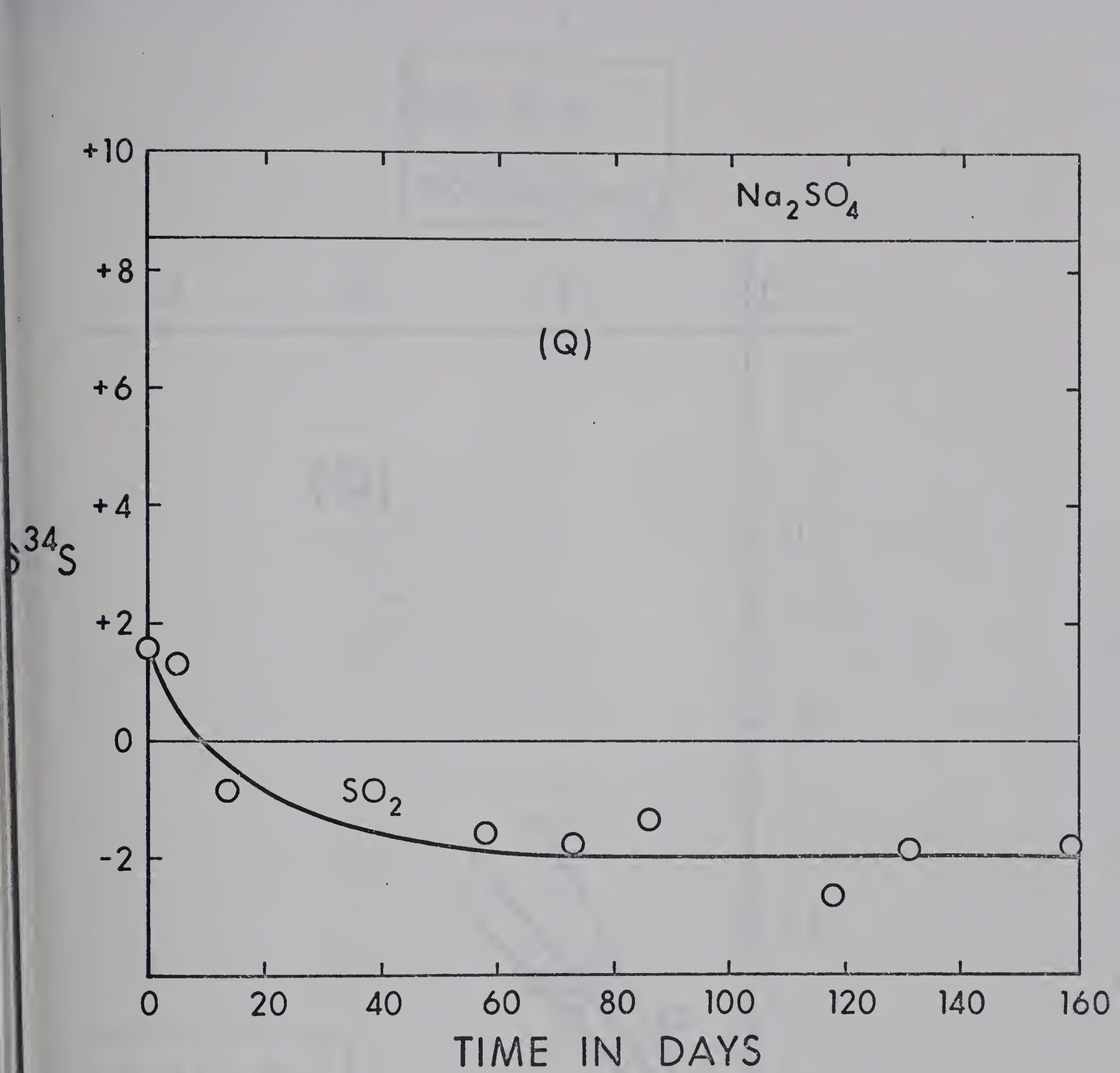
$\delta^{34}S$ of Initial SO_2 = +1.59

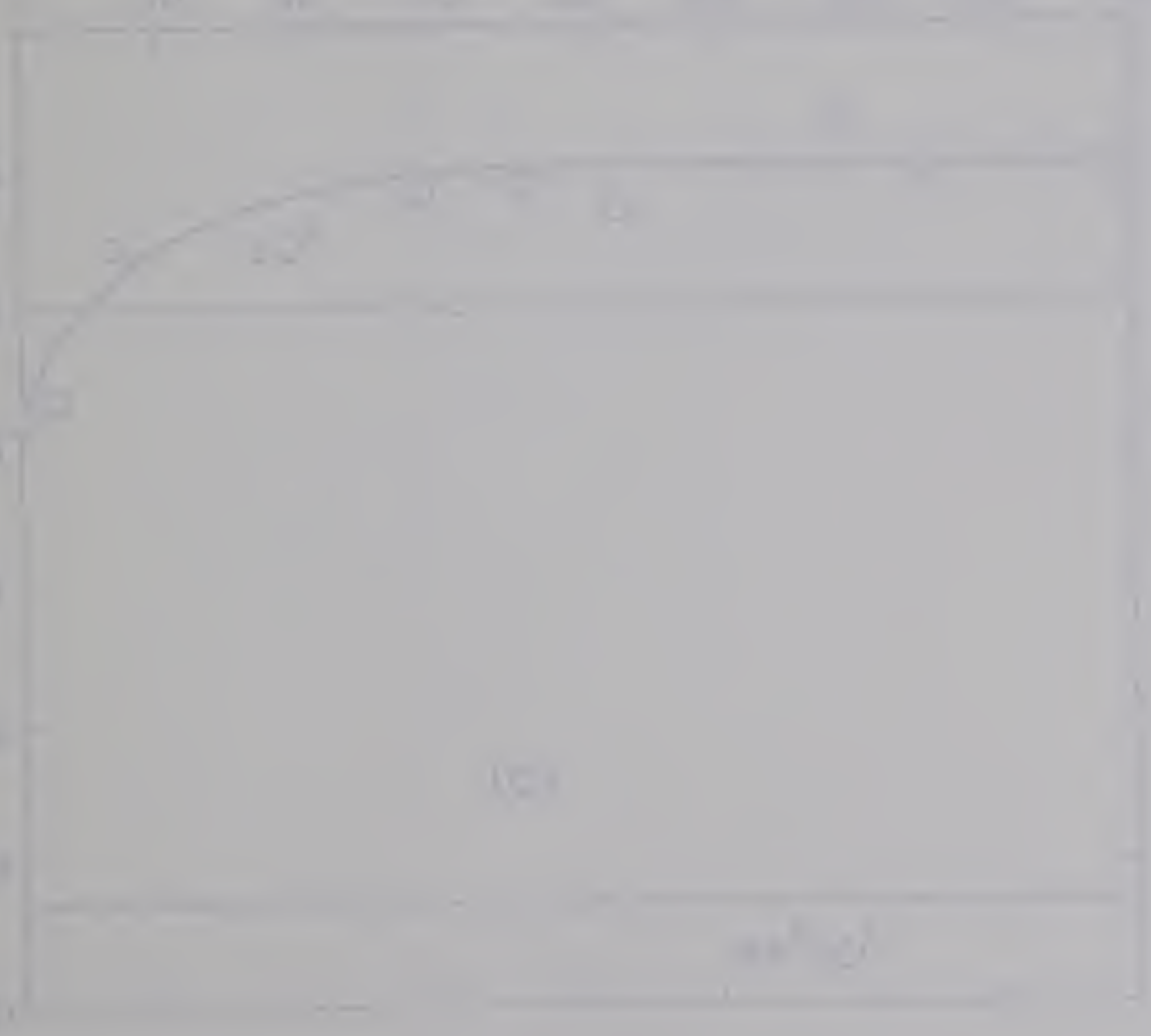
$\delta^{34}S$ of Initial Na_2SO_4 = +8.56

Sample	Time of Exchange in Days	$\delta^{34}S$ of SO_2
Q-1	Start 5 Feb. 1966	+1.30
Q-2	14	-0.90
Q-3	58	-1.56
Q-4	73	-1.73
Q-5	86	-1.33
Q-6	118	-2.64
Q-7	131	-1.87
Q-8	159	-1.70

FIGURES

XIX and XIX-a: Series (Q), Equilibration of Na_2SO_4 (in solution) and SO_2 at 100°C, SO_2 pressure 200 mm Hg.


+10
+8
+6
+4
+2
0
-2
$\delta^{34}S$
Na_2SO_4
(Q)
SO_2
0
20
40
60
80
100
120
140
160
TIME IN DAYS



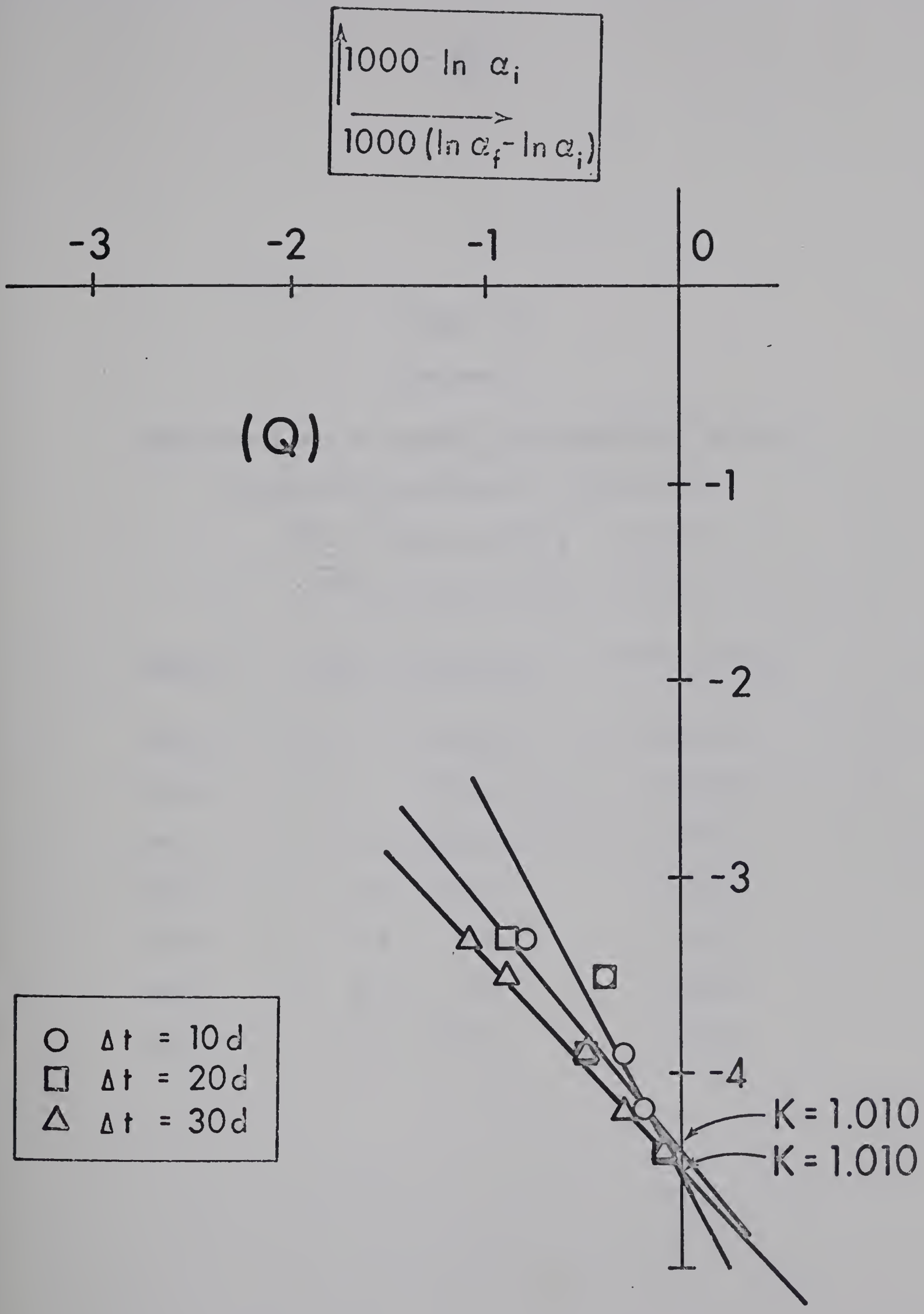

1000 ln α_i
1000 (ln α_f - ln α_i)
-3
-2
-1
0
(Q)
-1
-2
-3
-4
K = 1.010
K = 1.010
○ Δt = 10 d
□ Δt = 20 d
△ Δt = 30 d



TABLE XX

Series M

Equilibration of $NaHSO_3$(soln) and SO_2 at 80°C

(Initial SO_2 pressure = 130 mm Hg)

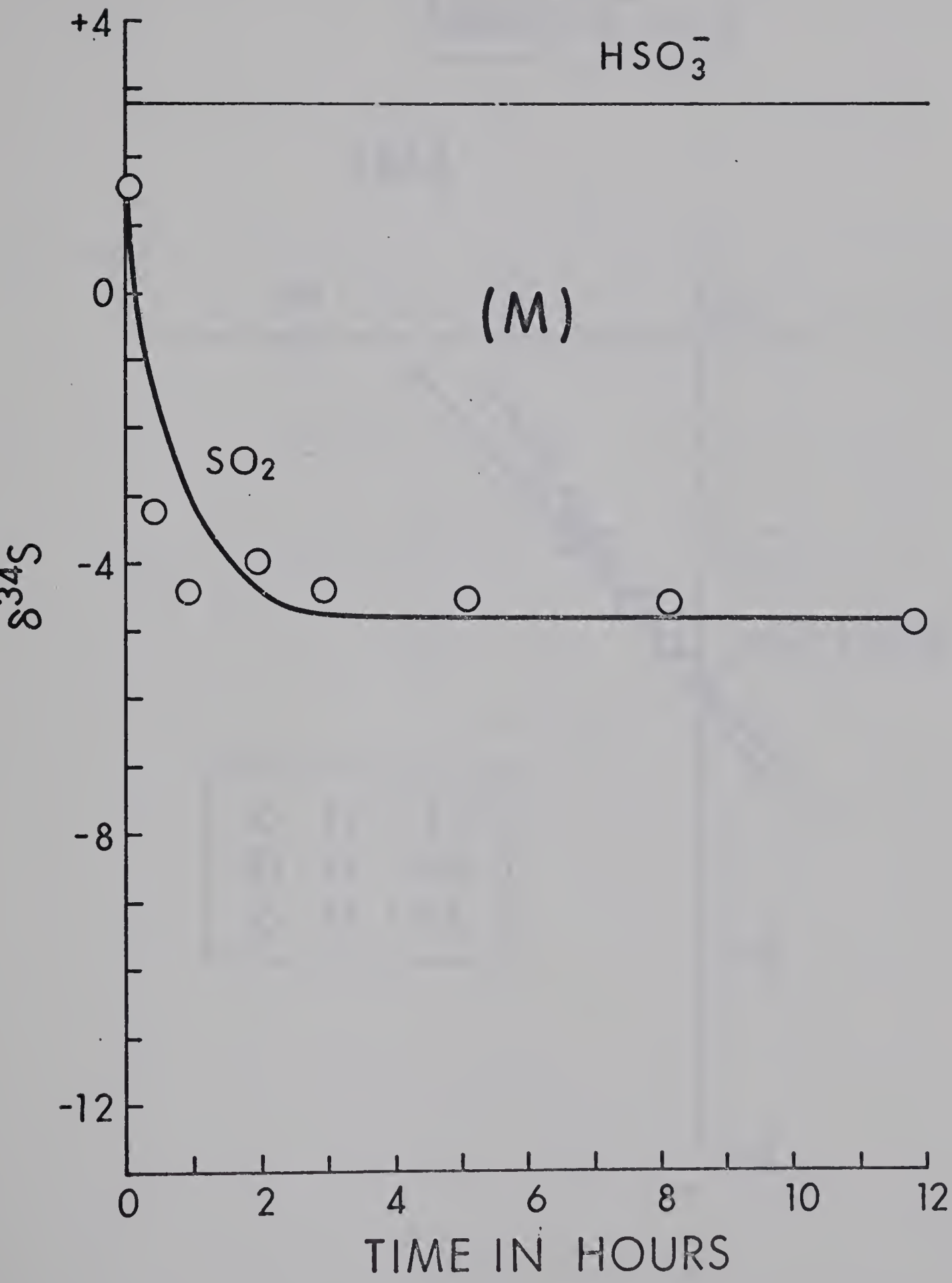
$\delta^{34}S$ of Initial HSO_3^- = +2.76

$\delta^{34}S$ of Initial SO_2 = +1.59

Sample	Time of Exchange	$\delta^{34}S$ of SO_2
M-1	23 m	-3.24
M-2	56 m	-4.44
M-3	1 h - 56 m	-3.98
M-4	2 h - 56 m	-4.40
M-5	5 h - 6 m	-4.54
M-6	8 h - 6 m	-4.58
M-7	11 h - 48 m	-4.93

FIGURES

XX and XX-a: Series (M), Equilibration of $NaHSO_3$ (in solution) and SO_2 at 80°C, SO_2 pressure 130 mm Hg.


+4
0
-4
-8
-12
$\delta^{34}S$
HSO_3^-
(M)
SO_2
0
2
4
6
8
10
12
TIME IN HOURS



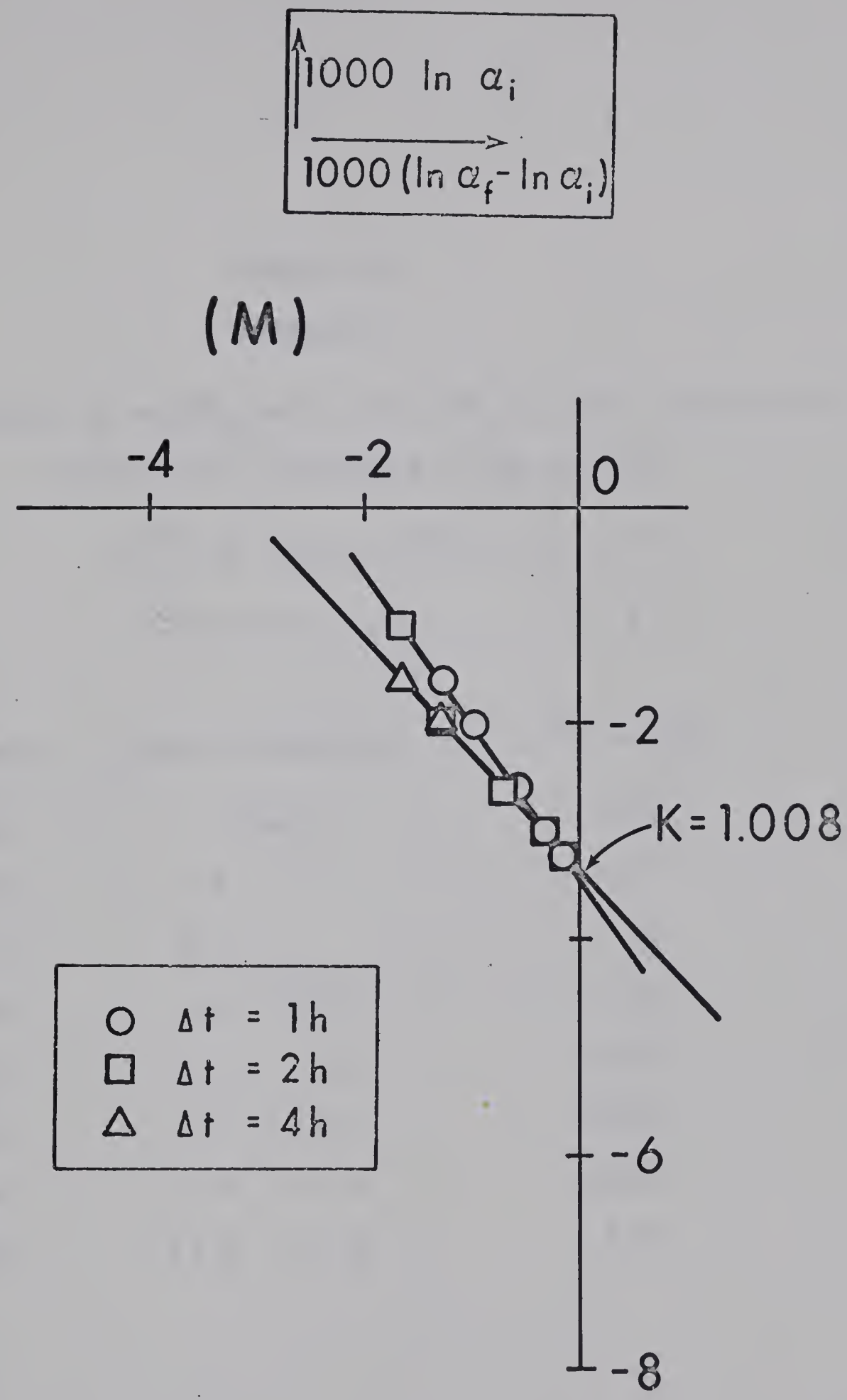

1000 ln α_i
1000 (ln α_f - ln α_i)
(M)
-4
-2
0
-2
K=1.008
-6
-8
○ Δt = 1h
□ Δt = 2h
△ Δt = 4h



TABLE XXI

Series N

Equilibration of $NaHSO_3$(soln) and SO_2 at Room Temperature

(Initial SO_2 pressure = 200 mm Hg)

$\delta^{34}S$ of Initial HSO_3^- = +2.76

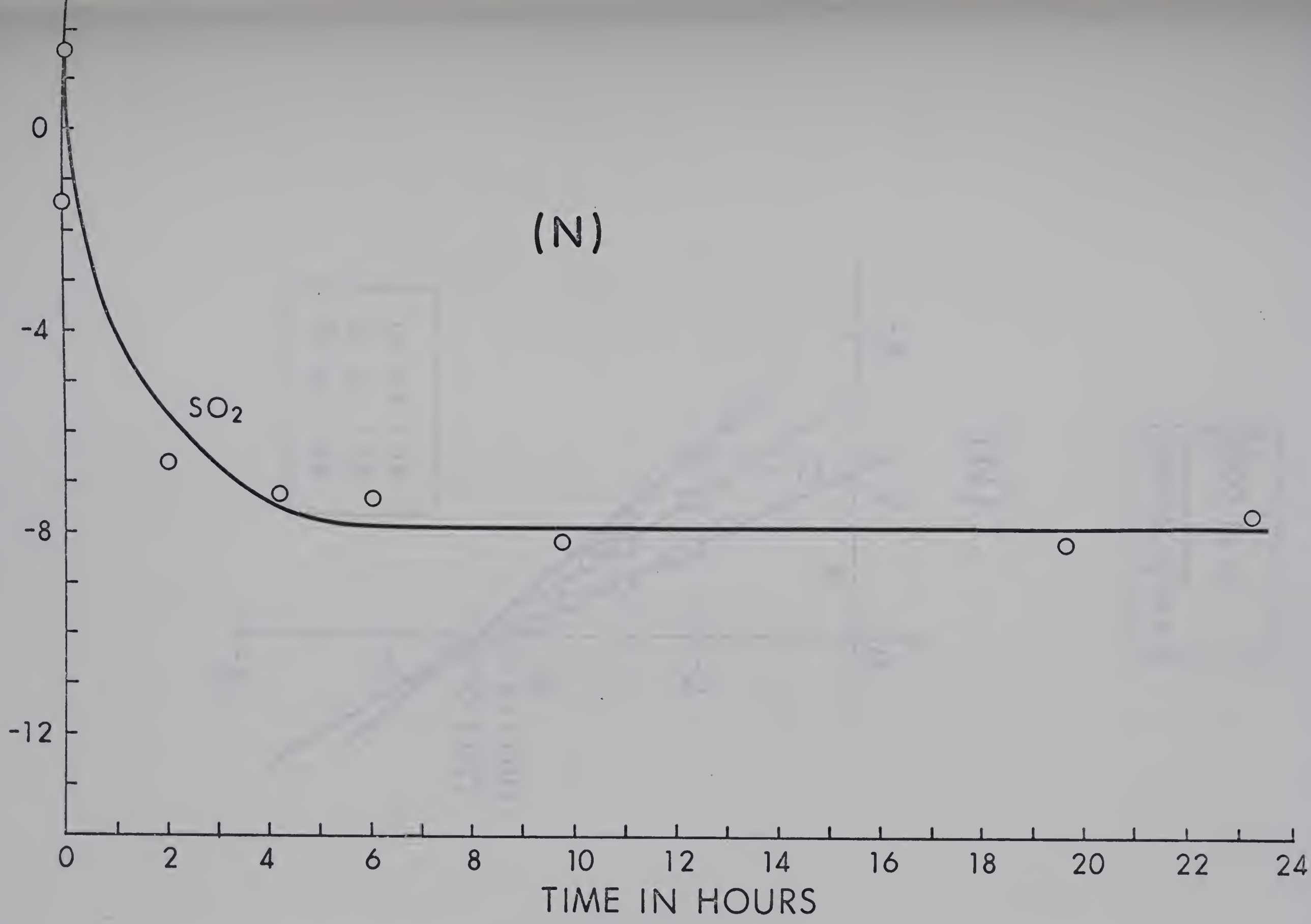
$\delta^{34}S$ of Initial SO_2 = +1.59

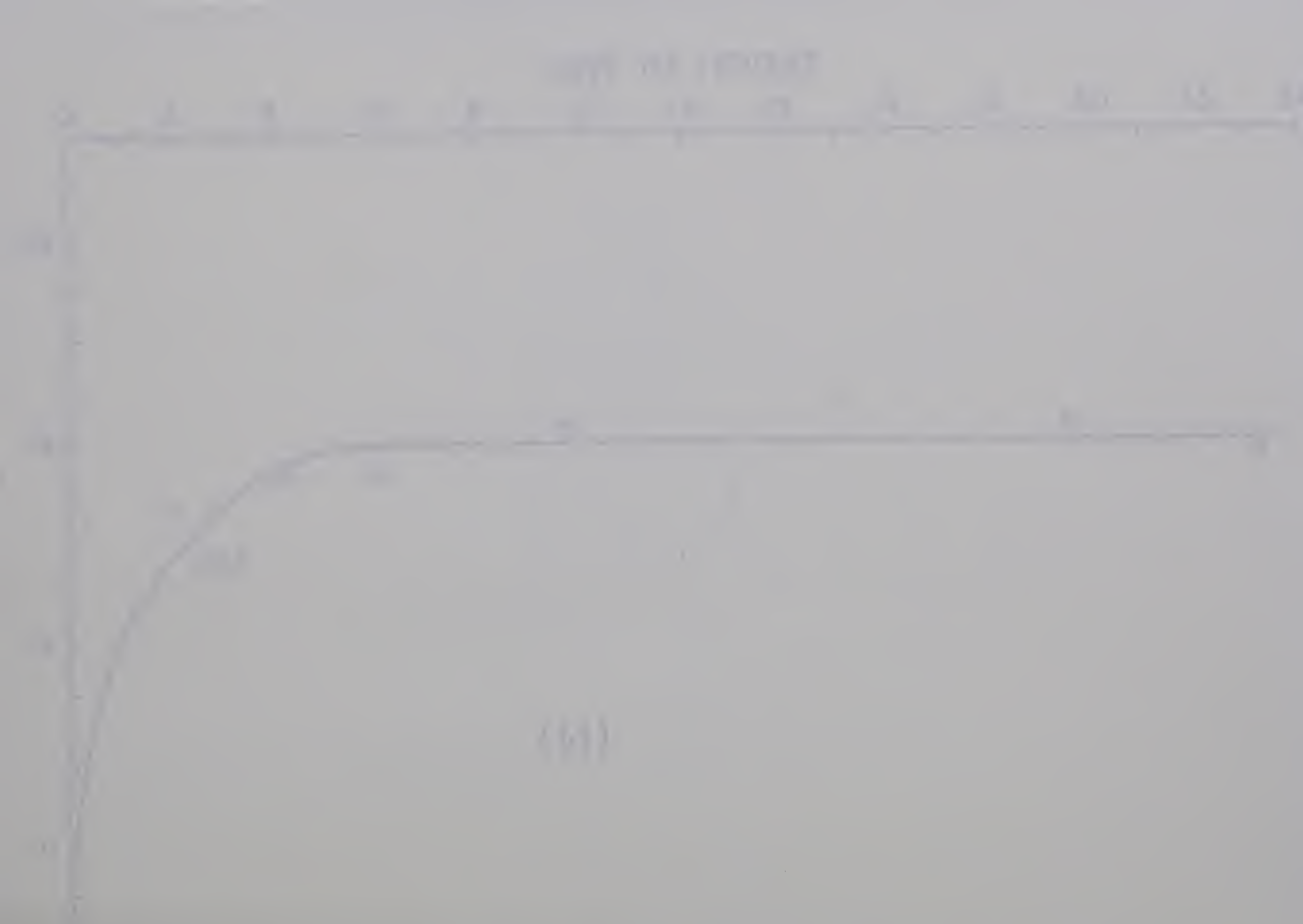
Sample	Time of Exchange	$\delta^{34}S$ of SO_2
N-1	Start	-1.40
N-2	1 h	-5.12
N-3	2 h	-6.60
N-4	4 h - 12 m	-7.22
N-5	6 h - 2 m	-7.29
N-6	9 h - 47 m	-8.16
N-7	19 h - 37 m	-8.18
N-8	23 h - 17 m	-7.57

FIGURES

XXI and XXI-a: Series (N), Equilibration of $NaHSO_3$ (in solution) and SO_2 at room temperature, SO_2 pressure 200 mm Hg.

(N)





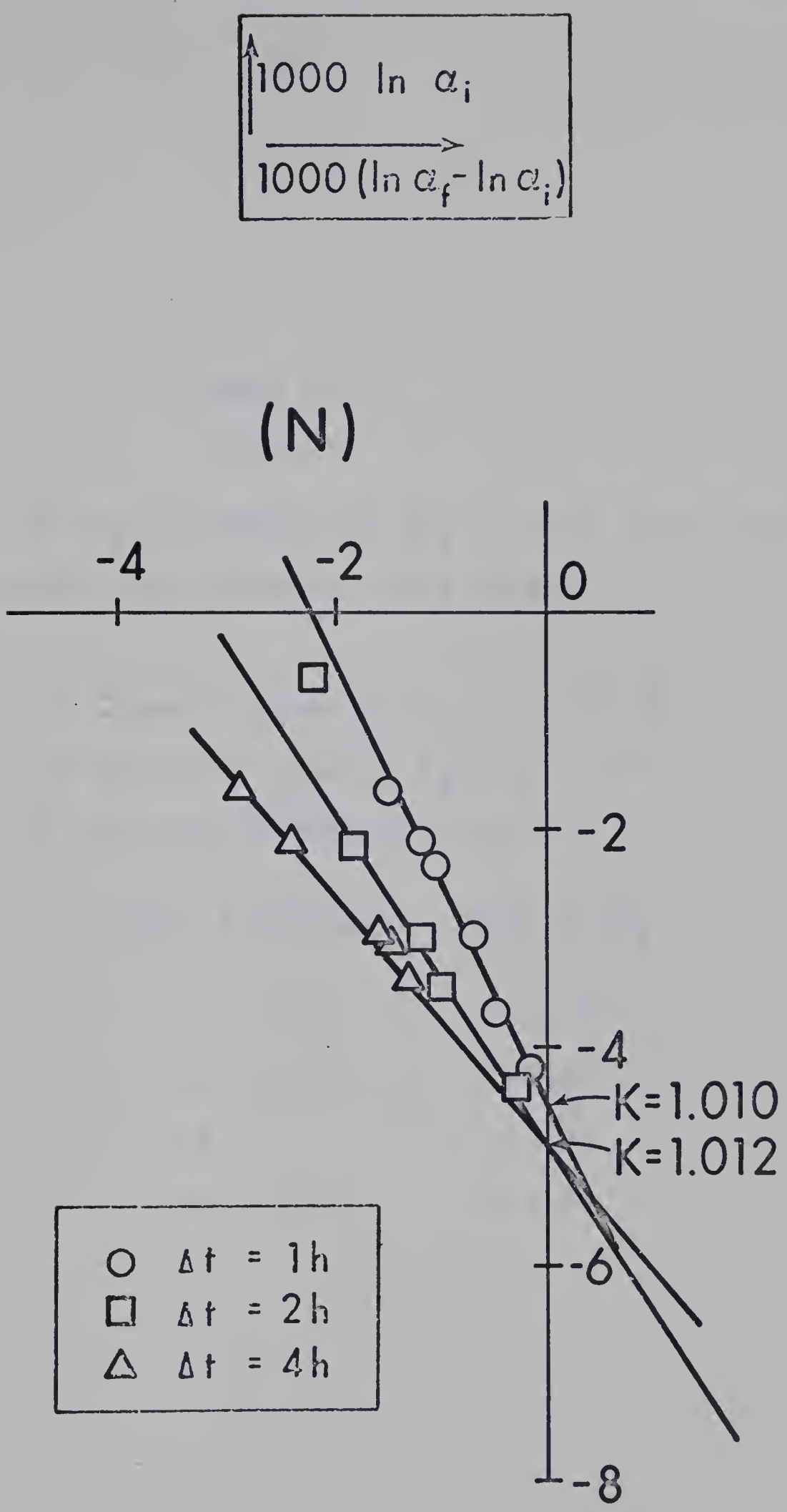

1000 ln α_i
1000 (ln α_f - ln α_i)
(N)
-4
-2
0
-2
-4
-6
-8
K=1.010
K=1.012
○ Δt = 1h
□ Δt = 2h
△ Δt = 4h



TABLE XXII

Series R

Equilibration of $Na_2S_2O_3$(soln) and SO_2 at Room Temperature

(Initial SO_2 pressure = 200 mm Hg)

$\delta^{34}S$ of Ligand S-atom in S_2O_3 = +9.85

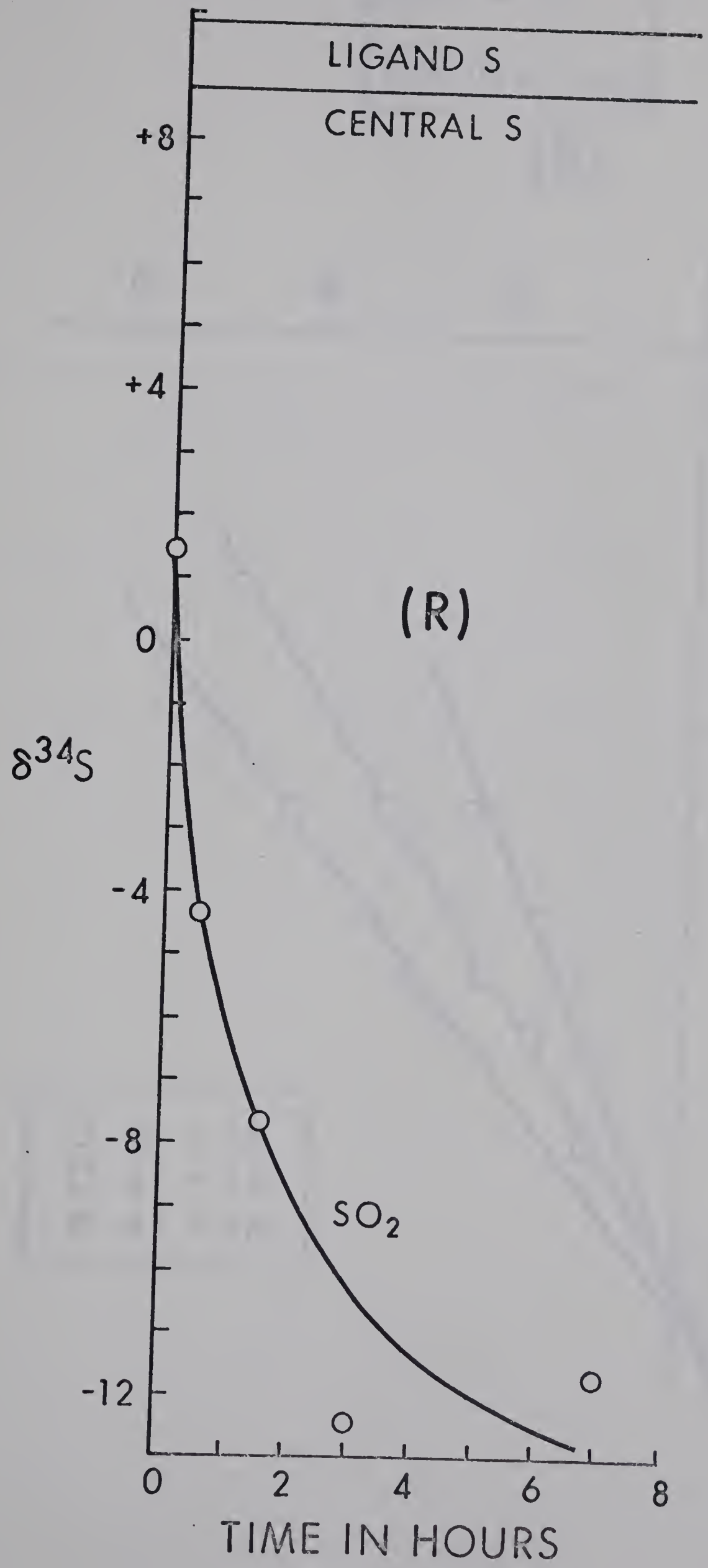
$\delta^{34}S$ of Central S-atom of S_2O_3 = +8.77

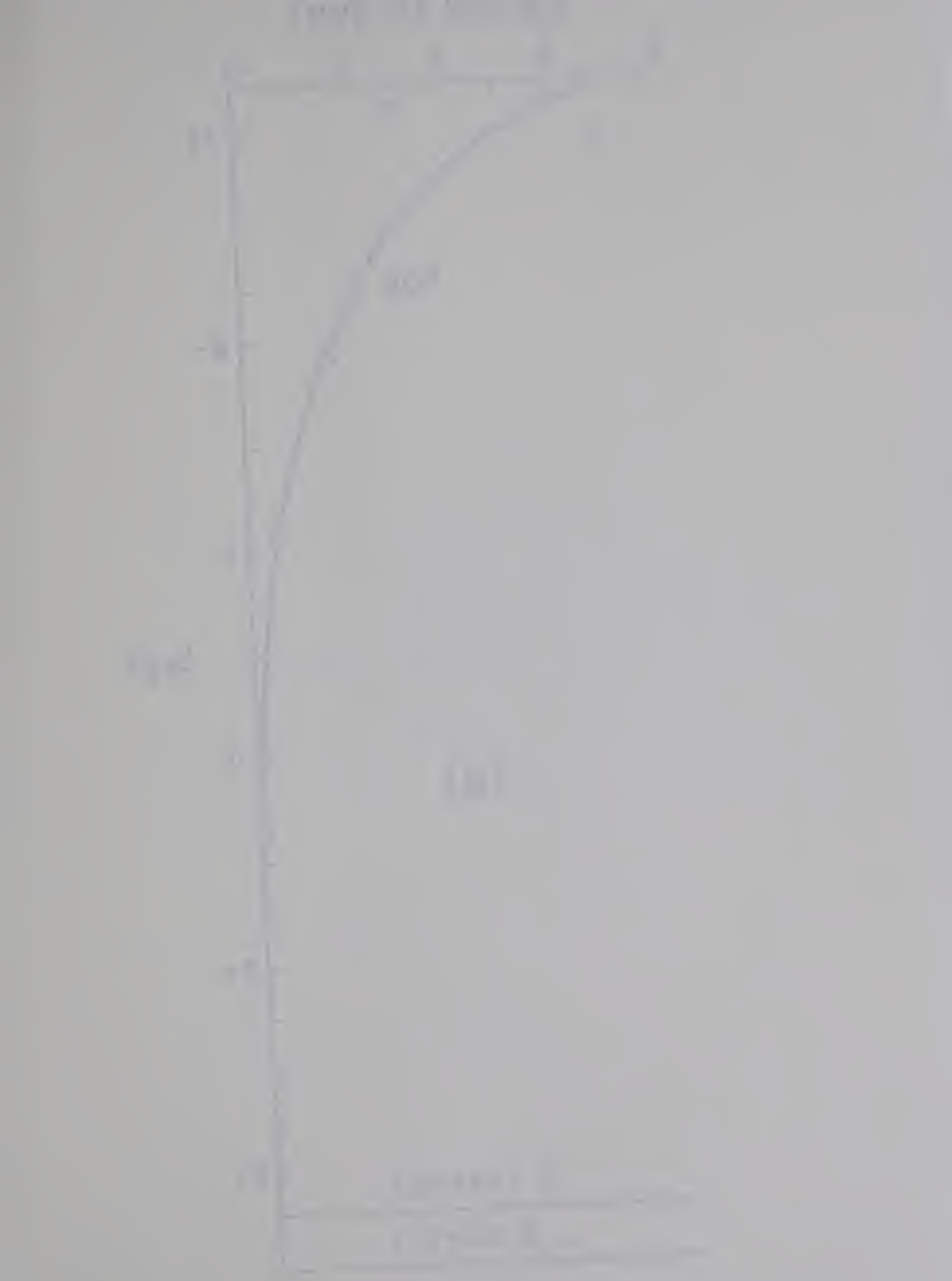
$\delta^{34}S$ of S^O produced in reaction vessel = -0.45

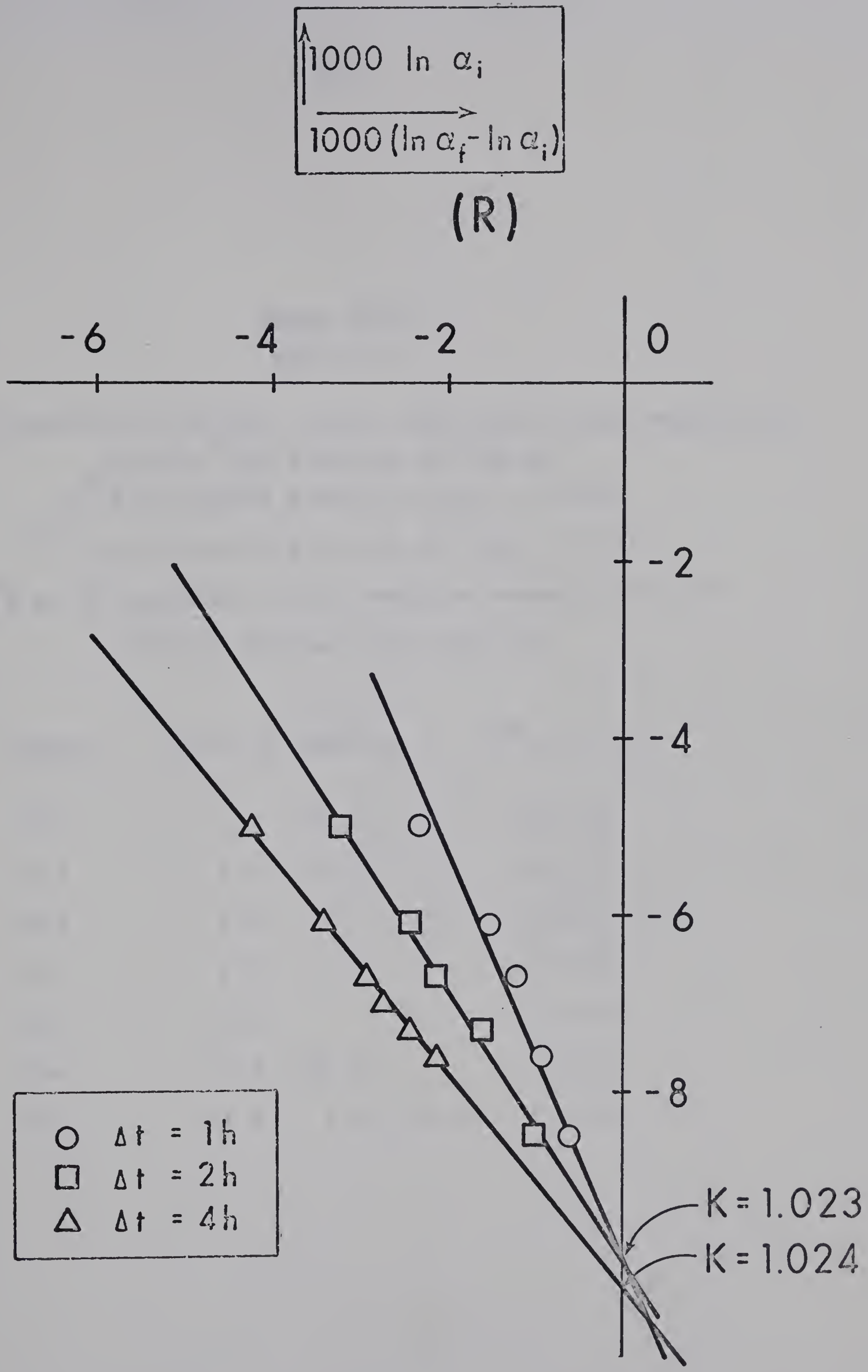
Sample	Time of Exchange	$\delta^{34}S$ of SO_2
R-1	30 m	-4.35
R-2	1 h - 31 m	-7.65
R-3	3 h	-12.48
R-4	7 h	-11.68

FIGURES

XXII and XXII-a: Series (R), Equilibration of $Na_2S_2O_3$ (in solution) and SO_2 at room temperature, SO_2 pressure 200 mm Hg.


LIGAND S
CENTRAL S
+8
+4
0
-4
-8
-12
$\delta^{34}S$
(R)
SO_2
0
2
4
6
8
TIME IN HOURS




1000 ln α_i
1000 (ln α_f - ln α_i)
(R)
-6
-4
-2
0
-2
-4
-6
-8
K = 1.023
K = 1.024
○ Δt = 1h
□ Δt = 2h
△ Δt = 4h

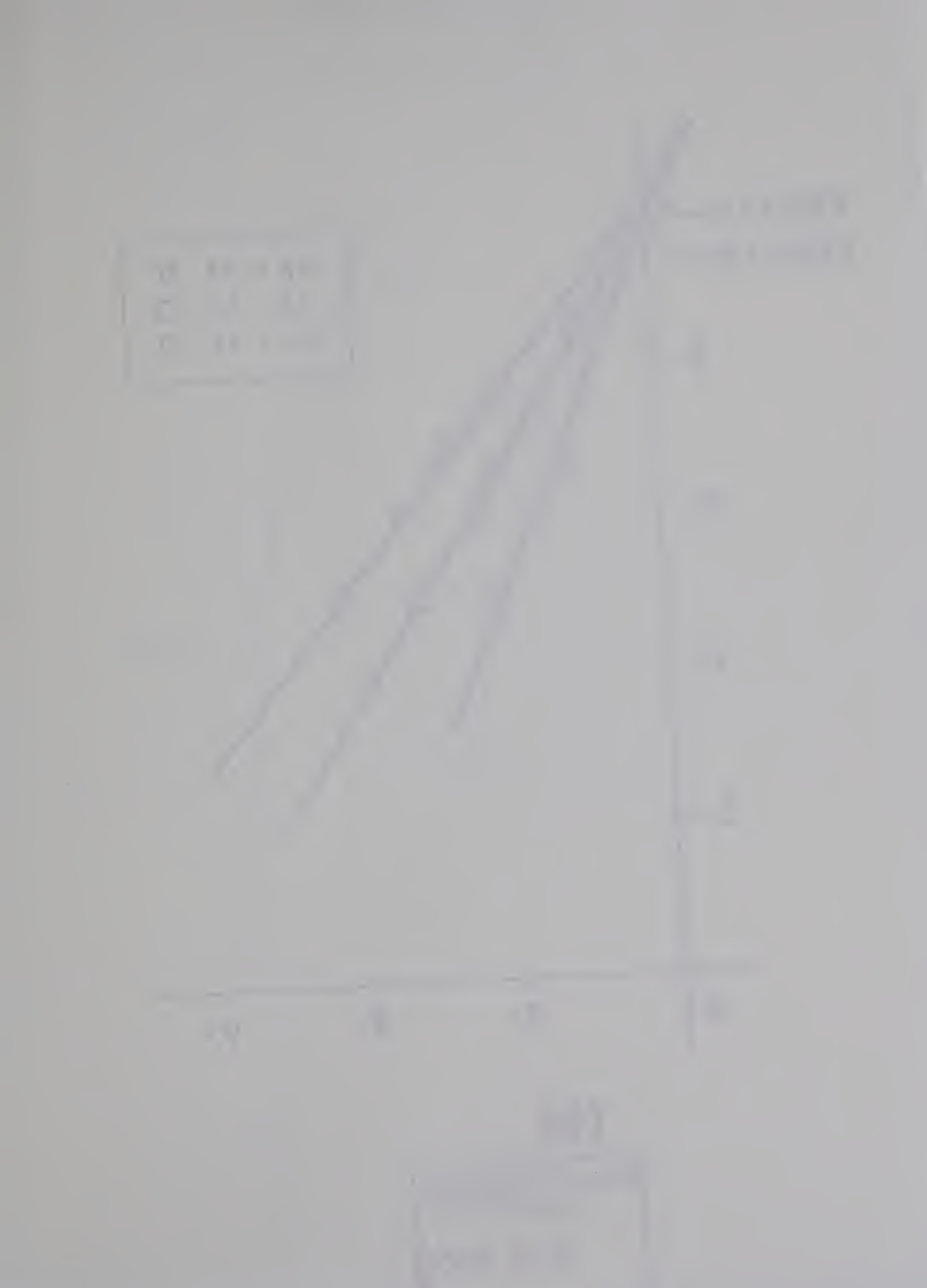


TABLE XXIII

Series S

Equilibration of $Na_2S_2O_3$ (soln) and H_2S at Room Temperature
(Initial H_2S pressure 200 mm Hg)

$\delta^{34}S$ of Ligand S-atom of S_2O_3 = +9.85

$\delta^{34}S$ of the Central S-atom of S_2O_3 = +8.77

$\delta^{34}S$ of S^0 produced in the reaction vessel = +13.40

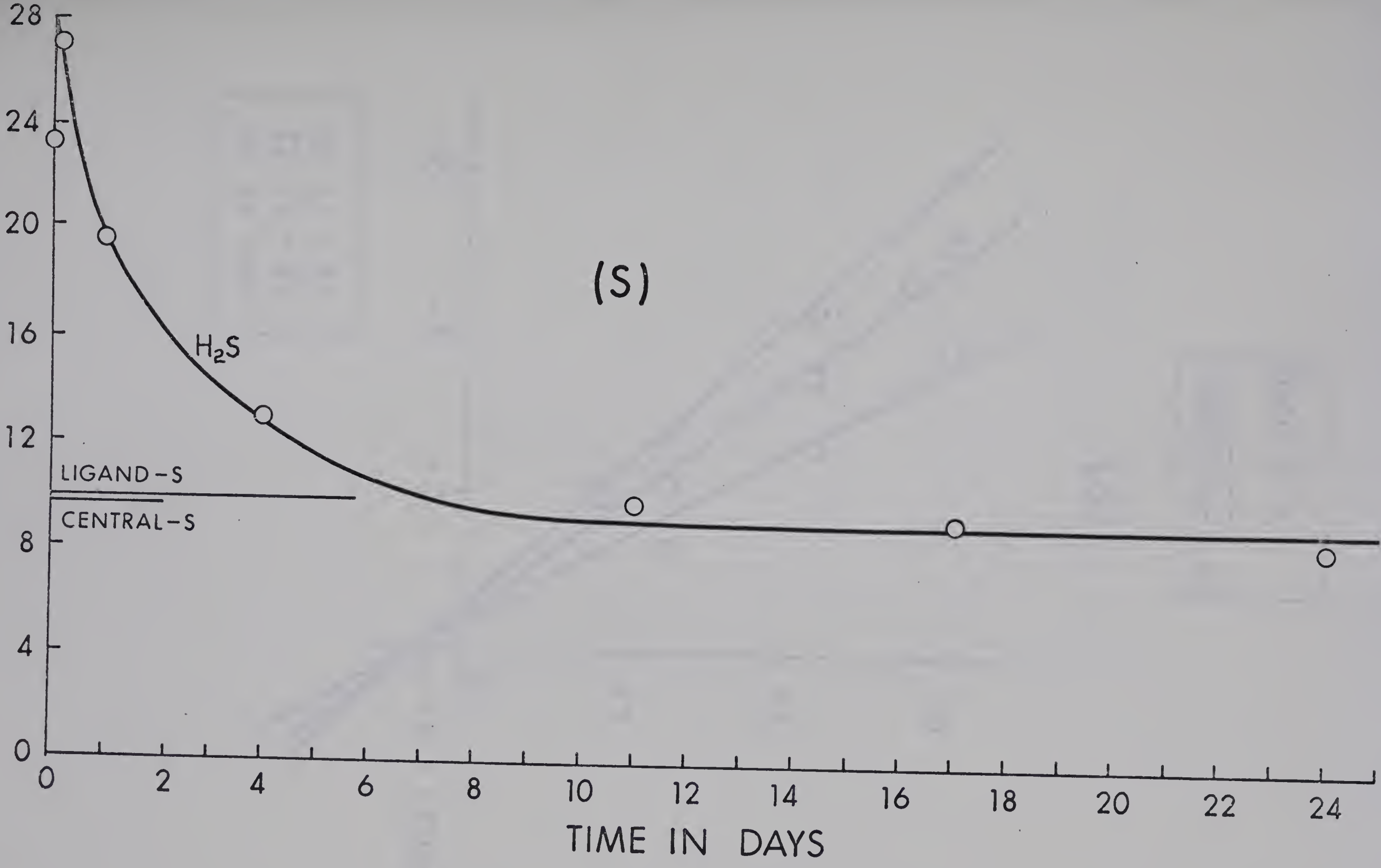
$\delta^{34}S$ of Initial H_2S = +22.62

Sample	Time of Exchange	$\delta^{34}S$ of H_2S
S-1	20 m	+20.85
S-2	1 h - 20 m	+26.97
S-3	1 d	+19.57
S-4	4 d	+12.92
S-5	11 d	+ 9.79
S-6	17 d - 40 m	+ 9.21
S-7	24 d - 1 h - 10 m	+ 8.42

FIGURES

XXIII and XXIII-a: Series (S), Equilibration of $Na_2S_2O_3$ (in solution) and H_2S at room temperature, H_2S pressure 200 mm Hg.

(S)


28
24
20
16
12
8
4
0
$\delta^{34}S$
H_2S
LIGAND-S
CENTRAL-S
0
2
4
6
8
10
12
14
16
18
20
22
24
TIME IN DAYS

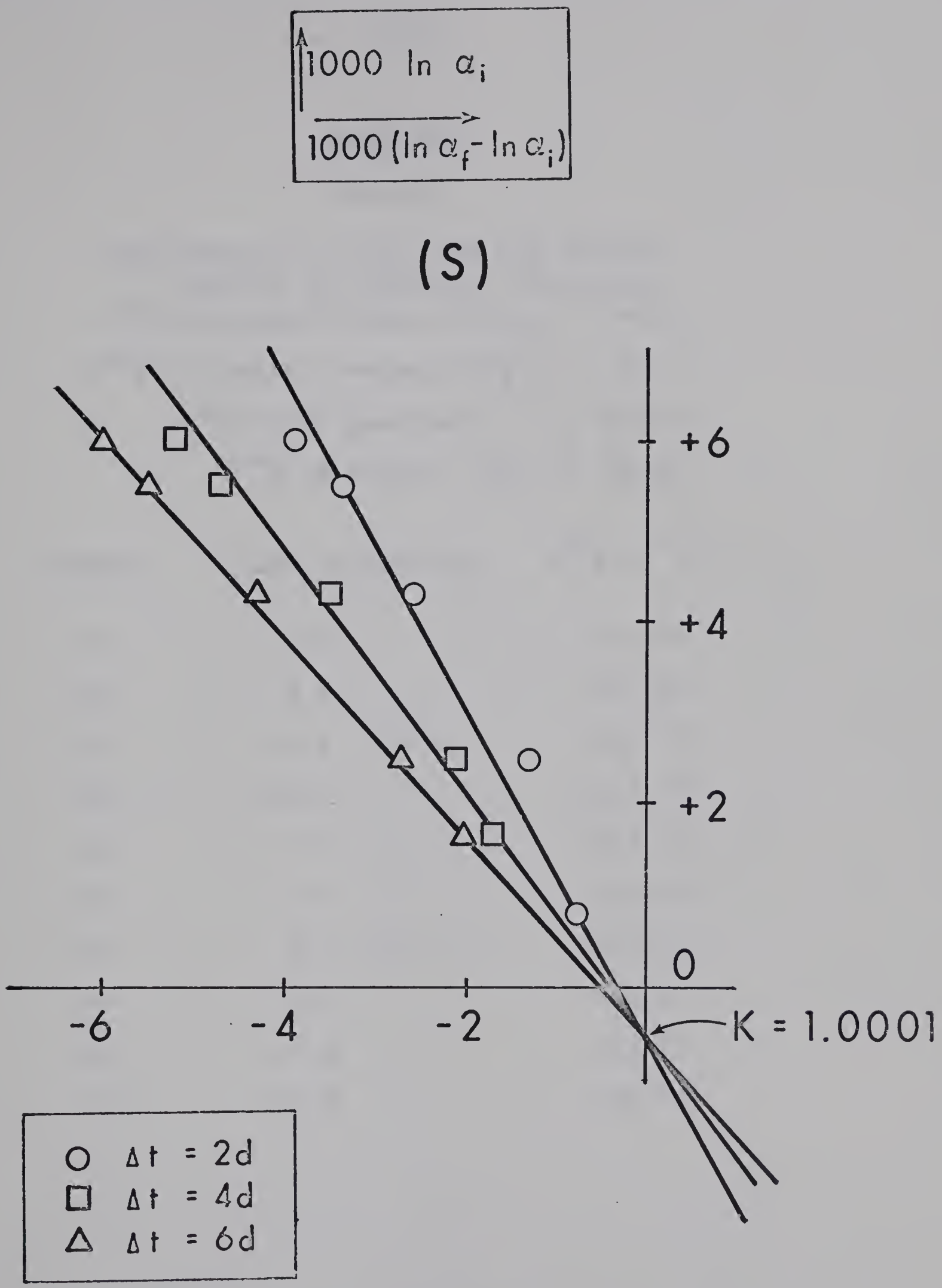

1000 ln α_i
1000 (ln α_f - ln α_i)
(S)
+6
+4
+2
0
-6
-4
-2
K = 1.0001
○ Δt = 2d
□ Δt = 4d
△ Δt = 6d

TABLE XXIV

Series U

Equilibration of S_2O_3 and H_2S at 60°C
(Initial H_2S pressure 200 mm Hg)

$\delta^{34}S$ of Ligand S-atom of S_2O_3 = +9.85

$\delta^{34}S$ of Central S-atom of S_2O_3 = +8.77

$\delta^{34}S$ of S^0 produced = +10.66

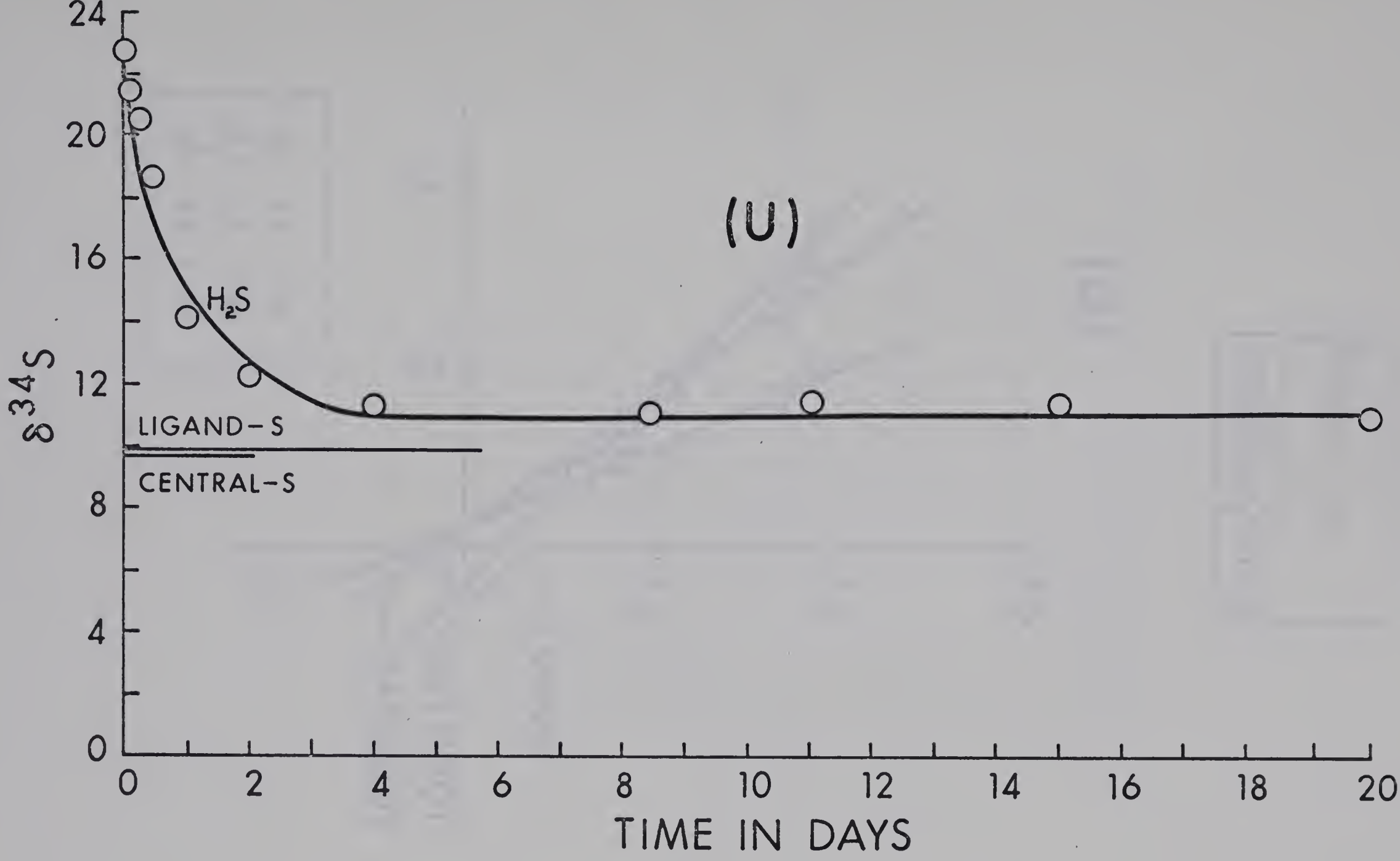
$\delta^{34}S$ of initial H_2S = +22.62

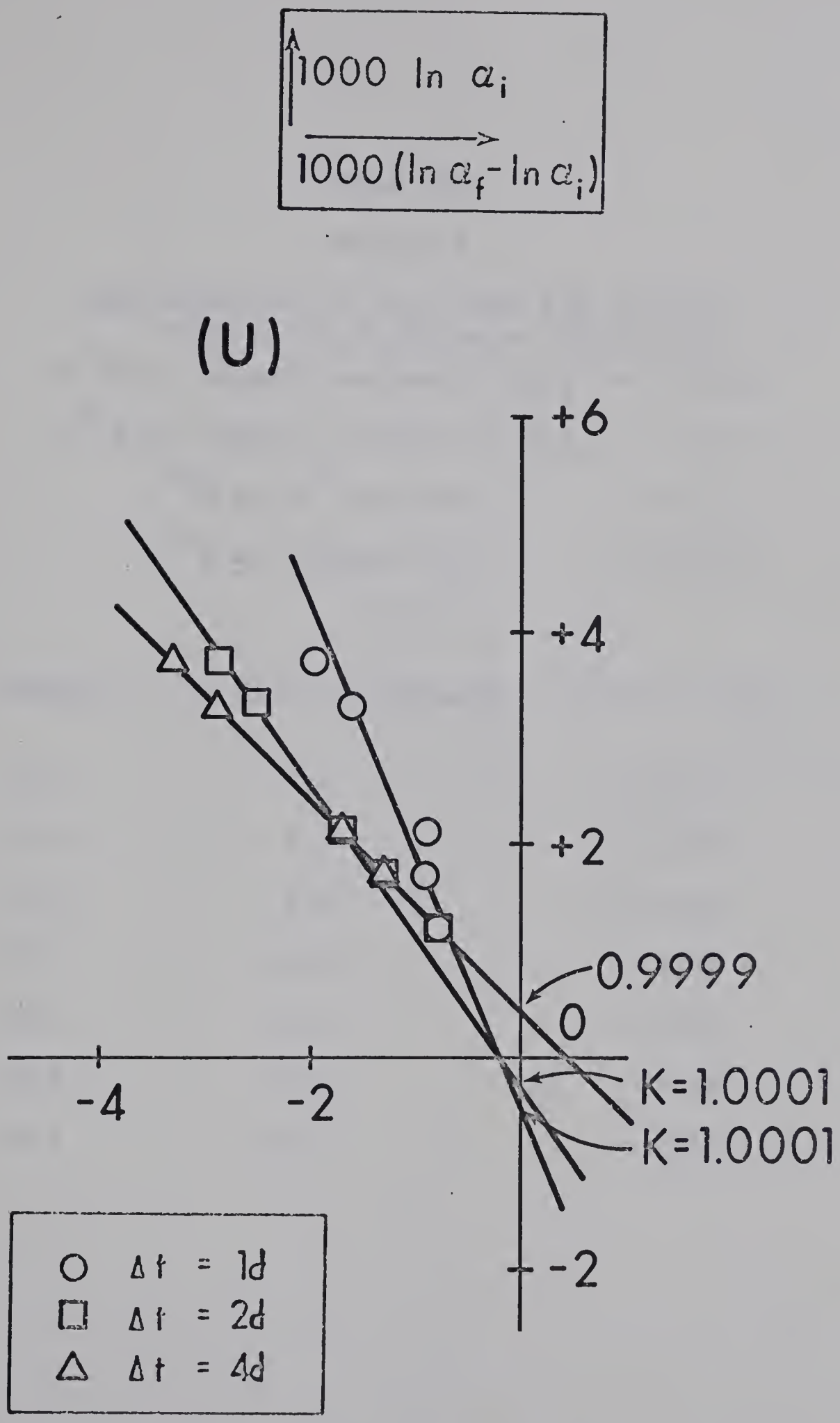
Sample	Time of Exchange	$\delta^{34}S$ of H_2S
U-1	2 h	+21.38
U-2	6 h	+20.38
U-3	10 h - 35 m	+18.58
U-4	24 h	+14.09
U-5	2 d	+12.25
U-6	4 d	+11.29
U-7	8 d - 10 h	+11.14
U-8	11 d	+11.37
U-9	15 d	+11.35
U-10	20 d	+10.93

FIGURES

XXIV and XXIV-a: Series (U), Equilibration of $Na_2S_2O_3$ (in solution) and H_2S at 60°C. H_2S pressure 200 mm Hg.

(U)


24
20
16
12
8
4
0
$\delta^{34}S$
H_2S
LIGAND–S
CENTRAL–S
0
2
4
6
8
10
12
14
16
18
20
TIME IN DAYS


1000 ln α_i
1000 (ln α_f - ln α_i)
(U)
+6
+4
+2
0
-2
-4
-2
0.9999
K=1.0001
K=1.0001
Δt = 1d
Δt = 2d
Δt = 4d

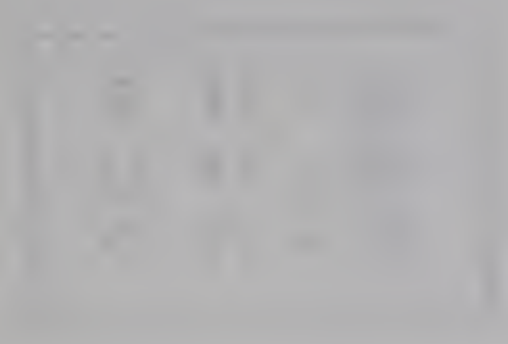




TABLE XXV

Series T

Equilibration of S_2O_3 and H_2S at 80°C
(Initial H_2S pressure 200 mm Hg)

$\delta^{34}S$ of Ligand S-atom of S_2O_3 = +9.85

$\delta^{34}S$ of Central S-atom of S_2O_3 = +8.77

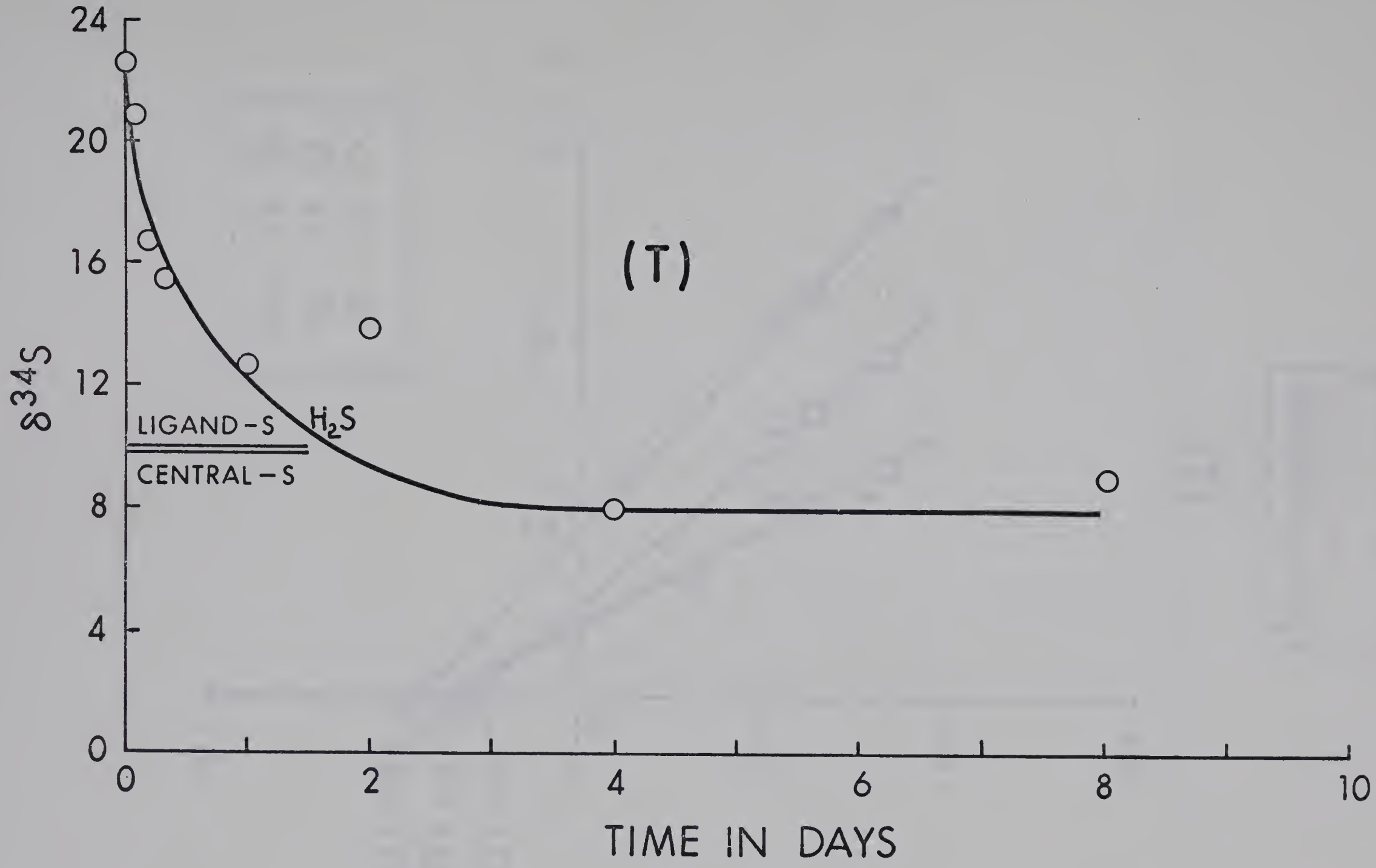
$\delta^{34}S$ of S^0 produced = +10.66

$\delta^{34}S$ of Initial H_2S = +22.62

Sample	Time of Exchange	$\delta^{34}S$ of H_2S
T-1	2 h	+20.87
T-2	5 h	+16.75
T-3	8 h	+15.45
T-4	24 h	+12.60
T-5	48 h	+12.90
T-6	96 h	+ 8.00
T-7	192 h	+ 9.00

FIGURES

XXV and XXV-a: Series (T), Equilibration of $Na_2S_2O_3$ (in solution) and H_2S at 80°C. H_2S pressure, 200 mm Hg.


24
20
16
12
8
4
0
$\delta^{34}S$
(T)
LIGAND-S
H_2S
CENTRAL-S
0
2
4
6
8
10
TIME IN DAYS



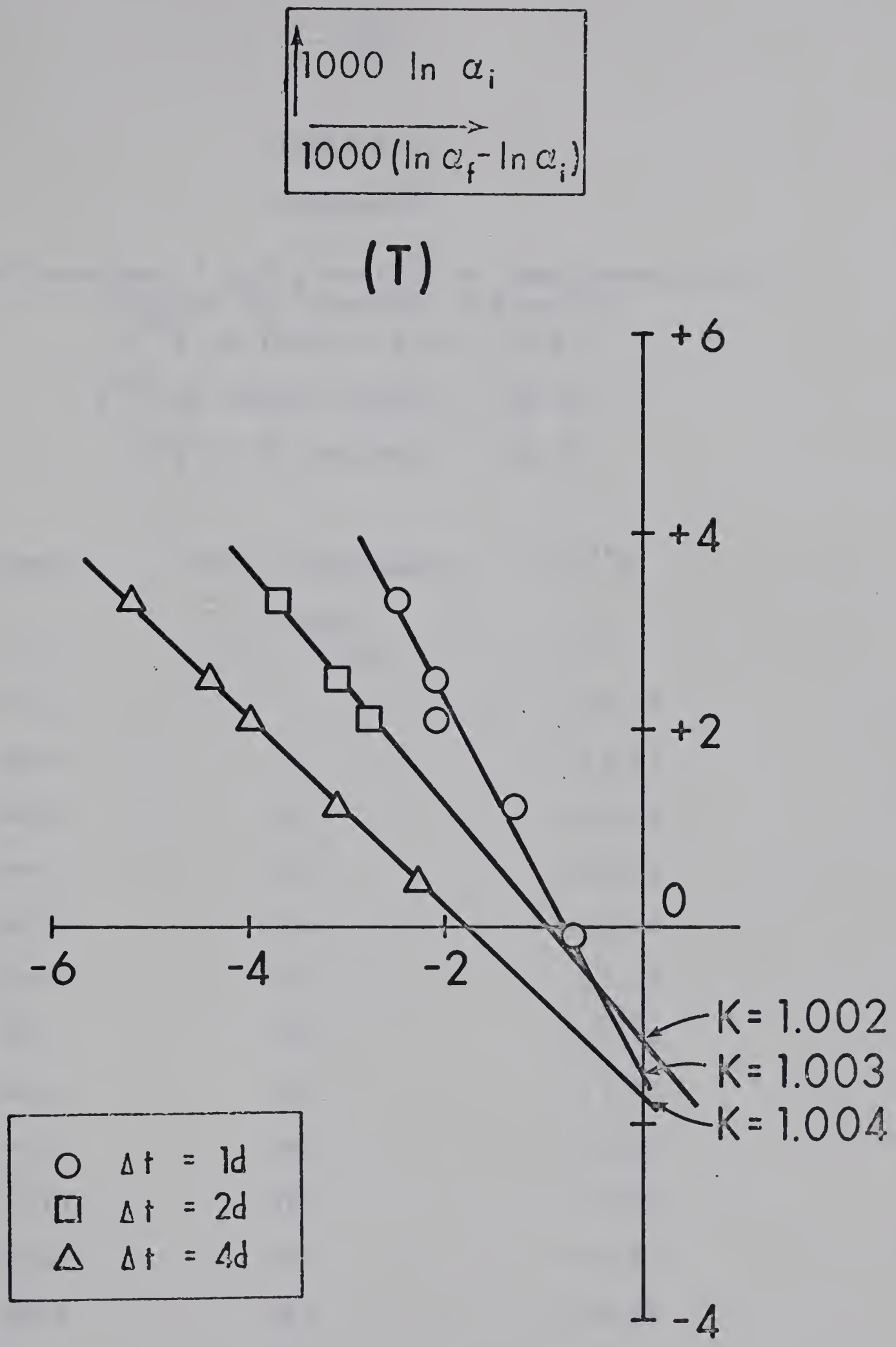

1000 ln α_i
1000 (ln α_f - ln α_i)
(T)
+6
+4
+2
0
-4
-6
-4
-2
K = 1.002
K = 1.003
K = 1.004
Δt = 1d
Δt = 2d
Δt = 4d



TABLE XXVI

Series W

Equilibration of H_2SO_4 and H_2S at Room Temperature
(Initial H_2S pressure 350 mm Hg)
$\delta^{34}S$ of Initial H_2S = +22.62
$\delta^{34}S$ of Initial H_2SO_4 = - 0.57
$\delta^{34}S$ of S° produced = +14.01

Sample	Time of Exchange in Days	$\delta^{34}S$
W-1	4	-18.30
W-2	87	-18.52
W-3	126	-17.84
W-4	181	-16.52
W-5	183	-17.84
W-6	304	-17.53
W-7	338	-17.26
W-8	368	-17.36
W-9	403	-17.84
W-10	428	-17.52
W-11	582	-18.87
W-12	611	-19.55
W13	640	-19.46

TABLE XXVII

Series X

Equilibration of H_2SO_4 and H_2S at 60°C
(Initial H_2S pressure 350 mm Hg)

$\delta^{34}S$ of Initial H_2S = +22.62

$\delta^{34}S$ of Initial H_2SO_4 = - 0.57

$\delta^{34}S$ of S^o produced = +19.16

Sample	Time of Exchange in Days	$\delta^{34}S$
X-1	55	-18.11
X-2	155	-18.19
X-3	224	-18.15
X-4	261	-18.50
X-5	297	-18.40
X-6	326	-17.80
X-7	366	-18.07
X-8	484	-17.64

TABLE XXVIII

Exchanges with Elemental Sulphur

60°C		Room Temperature	
Time of Exchange in Days	$\delta^{34}S$	Time of Exchange in Days	$\delta^{34}S$
$Na_2SO_4 + S^0$:-		$Na_2SO_4 + S^0$:-	
92	-0.37	92	+0.42
139	+5.69	224	+2.38
224	+0.06	286	-0.06
$H_2SO_4 + S^0$:-		$H_2SO_4 + S^0$:-	
34	-0.42	182	-0.43
182	+0.07	314	-0.06
373	+0.22		
$Na_2SO_3 + S^0$:-		$Na_2SO_3 + S^0$:-	
34	-0.52	35	-0.71
182	-0.94	182	-2.60
373	-0.09	314	-1.24
$Na_2S_2O_3 + S^0$:-		$Na_2S_2O_3 + S^0$:-	
34	-0.75	35	-0.22
182	+0.27	182	+0.94
304	+0.19	314	+0.07

TABLE XXIX

APPROXIMATE HALF-TIMES FOR SULPHUR ISOTOPE EXCHANGE BETWEEN H_2SO_4 AND SO_2

Temperature °C	Series	SO_2 Pressure mm Hg	O_2 Pressure mm Hg	Half Time
265	A	10	-	1 h - 6 m
265	B	100	-	50 m
265	C	200	-	1 h
265	D	300	-	1 h
265	E	400	-	58 m
254	P	100	-	2 h
240	F	10	-	1 h - 30 m
240	G	100	-	1 h - 32 m
240	H	200	200 (AIR)	1 h - 53 m
240	I	400	-	2 h - 40 m
240	J	100	10	2 h - 22 m
150	O	350	-	25 d

FIGURE XXVI

Comparison of the Experimental

K-values for the Exchange

$$H_2{}^{32}SO_4 + {}^{34}SO_2 \overset{K}{\rightleftharpoons} H_2{}^{34}SO_4 + {}^{32}SO_2$$

(This work and Dunford et al, 1957)

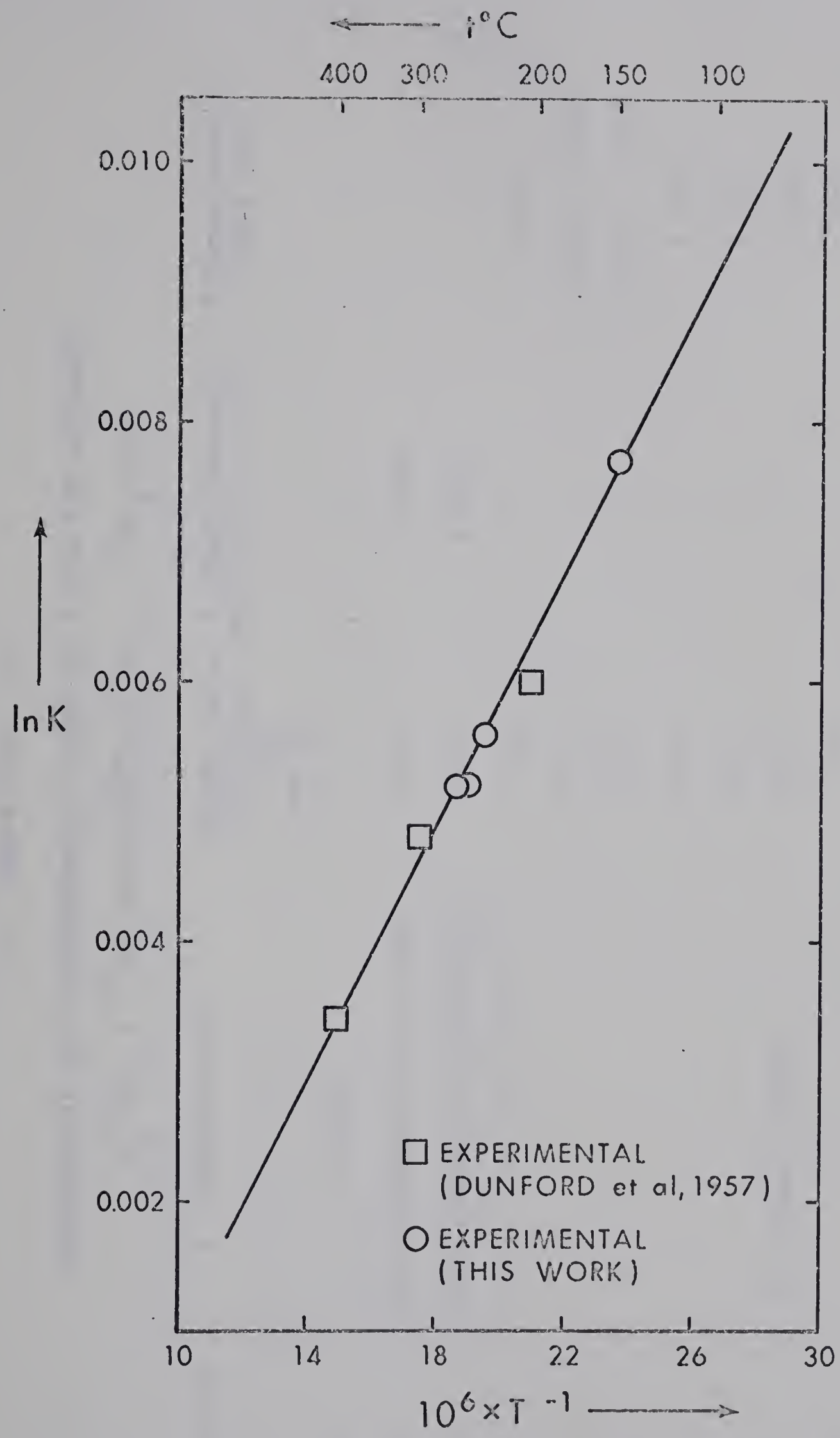

t°C
400
300
200
150
100
0.010
0.008
0.006
0.004
0.002
ln K
EXPERIMENTAL
(DUNFORD et al, 1957)
EXPERIMENTAL
(THIS WORK)
10
14
18
22
26
30
10⁶ × T⁻¹



TABLE XXX

THEORETICAL AND EXPERIMENTAL VALUES OF K FOR THE EXCHANGE

$$H_2{}^{32}SO_4 + {}^{34}SO_2(gas) \underset{}{\overset{K}{\rightleftharpoons}} H_2{}^{34}SO_4 + {}^{32}SO_2(gas)$$

Temperature °C	K (Theoretical)	Approximate Pressure SO_2 mm Hg	K (Experimental) Dunford et al,1957	K(Experimental) This Work
500	1.006	-	-	-
400	1.009 (Dunford et al,1957)	570	1.008	-
300	1.012 (Dunford et al,1957)	570	1.011	-
265	-	10	-	1.012
265	-	100	-	1.010, 1.012
265	-	200	-	1.011, 1.012
265	-	300	-	1.012
265	-	400	-	1.012
254	1.016 (Sakai,1957)	100	-	1.012
240	-	10	-	1.012
240	-	100	-	1.012, 1,013
240	-	200 (AIR, 200mmHg)	-	1.016
240	-	400	-	1.014, 1.015, 1.016

TABLE XXXI (continued)

240		100 (O_2,10mmHg)	-	1.016
205	1.018 (Dunford et al,1957)	570	1.014	-
150	-	350	-	1.018
100	1.020 (Sakai, 1957)	-	-	-
50	1.024 (Sakai, 1957)	-	-	-
25	1.028 (Sakai, 1957)	-	-	-
	1.041 (Tudge and Thode,1950)			
0	1.046 (Tudge and Thode,1950)	-	-	-

TABLE XXX (continued)

240			100 (O_2,10mmHg)	-	1.016
205	1.018	(Dunford et al,1957)	570	1.014	-
150		-	350	-	1.018
100	1.020	(Sakai, 1957)	-	-	-
50	1.024	(Sakai, 1957)	-	-	-
25	1.028	(Sakai, 1957)	-	-	-
	1.041	(Tudge and Thode,1950)			
0	1.046	(Tudge and Thode,1950)	-	-	-

CHAPTER VIII

DISCUSSION

In this chapter, the results are summarized for the isotopic exchange systems studied. Comparison is made with theoretical calculations and data from other studies. Where it seems appropriate, comments are made about the relevance of the results to natural phenomena.

EXCHANGE BETWEEN $SO_2 \leftrightarrow H_2SO_4$ AND $SO_2 \leftrightarrow Na_2SO_4$ (SOLUTION)

The exchange between H_2SO_4 and SO_2 was studied using ^{35}S by Norris (1950) in the temperature range 100° to 210°C. The half-times for complete exchange were reported as 7.5 hours at 211°C, 6.2 days at 160°C, and 20.5 days at 137°C. Half times derived from the present experiments (analyses of the isotopic composition of SO_2 vs time curves) are summarized in Table XXIX. It is seen that the half times of Table XXIX are quite comparable to those found by Norris.

The effect of SO_2 pressure on the exchange rate is also seen in Table XXIX. Over the pressure range 10 mm to 400 mm Hg, the half-times are reasonably constant as shown by the series (A) to (E). It must be remembered that the $^{34}S/^{32}S$ composition of the SO_2 was monitored and this gives a measure of the <u>fraction</u> of sulphur isotopes exchanged in the SO_2 at any given time. Therefore, over the pressure range studied, the fraction

exchanged as a function of time was the same for all trials. This implies that at 400 mm Hg of SO_2, 40X as many sulphur atoms were exchanged as at a pressure of 10 mm Hg of SO_2. Therefore the exchange rate (no. of atoms exchanging per unit time) varies directly as the SO_2 pressure.

Our measured values of the equilibrium exchange constants can be compared to those of Dunford et al (1957). They studied this exchange mass spectrometrically at the temperatures 205°, 300° and 400°C. Their results agreed reasonably well with theoretical calculations based on sulphur isotope exchange between sulphate ion and sulphur dioxide.

In Table XXX and Figure XXVI the equilibrium constant determined experimentally in the present work are compared with the findings of Dunford et al (1957). It is seen that the agreement between the two studies is very good. One experimental difference is that Dunford et al (1957) used 100% sulphuric acid whereas the present experiment used 95.5 - 96.5% sulphuric acid.

In the series (H) and (J), air and oxygen were respectively introduced into the systems to see if the exchange rates were noticeably affected. There is no evidence that the presence of oxygen increased the rate of exchange (compare to series (F), (G), and (I)).

The run at 100°C does not give results consistent with the other runs or the theoretical expectations. Unfortunately, the isotopic determinations scattered very badly and one cannot draw a representative curve for analyses. Norris (1950) found that the half time for exchange at 101°C was 1.6 years so that during the time of the present experiment, it should have been possible to determine K. In the present case, it appears that the half time for the exchange is much longer. (Norris, 1950) suggested that the value of 1.6 years had a large error associated with it. Therefore, one would have to carry out the experiment for a much longer time to utilize the methods of this thesis effectively.

In Figure XVIII, there is evidence that SO_2 exchanged very slowly with solid Na_2SO_4 at 240°C. The extent of alteration of the $^{34}S/^{32}S$ composition of the SO_2 in this experiment should be dependent upon the area of sulphate exposure and the extent of exchange between the surface and interior sulphur atoms. If the mobility within the crystal were sufficiently high, the isotope effect should approach that obtained with sulphate ions in solution. On the other hand, if the interior mobility were slow, so that only surface atoms effectively exchanged with the SO_2, then the isotopic alteration of the SO_2 would be small. The results of

this experiment suggest that the latter case is more representative.

In case of Na_2SO_4 (in solution) in contact with SO_2 gas at 100°C, noticeable exchange was observed (Figure XIX.). The experimental value of K as found from Figure XIX-a is 1.010 which is not in good agreement with the theoretical values of 1.020 calculated by Sakai (1957) and 1.018 of Dunford et al (1957). It may be that equilibrium was not attained as suggested by Figure XIX in view of the scatter in the data. However, the uncertainty in the line drawn through the experimental points is much smaller than the 1 percent discrepancy between experiment and theory. In any case, it is quite obvious that exchange occurred and the isotope effect was significant.

One problem inherent in these and some of the other systems examined is the solubility of the gas component in the liquid phase. In the case of $H_2SO_4 \leftrightarrow SO_2$ equilibration, Dunford et al (1957) recovered only about one half of the sulphur dioxide. They boiled the sulphuric acid, however, to remove the dissolved SO_2 and examined it isotopically. It was about 0.1% enriched in ^{34}S with respect to the SO_2 previously recovered above the acid so that this error is relatively small in comparison to the isotope effects noted.

Another problem which arises during the mass spectrometric determinations, results from possible exchange of oxygen atoms between sulphuric acid and sulphur dioxide.

Mass 66 is comprised mainly of $^{34}S^{16}O^{16}O$ and $^{32}S^{16}O^{18}O$ and an $^{18}O/^{16}O$ correction must be applied to the mass spectrometric raw data. Theoretical calculations by Urey (1947) place the equilibrium constant for ^{16}O - ^{18}O exchange between SO_2 and $SO_4^=$ in the range 0.999 to 1.001 between 400° and 600°K. Therefore, this error is also small in comparison to the isotope effects observed.

The present study does not entirely elucidate the exchange mechanism. It does conclude (1) The exchange rate is directly proportional to the SO_2 pressure, (2) Exchange can occur with solid sulphate and sulphate ion in solution. From this it would appear that the reaction may not be noticeably accelerated by concentrated acid, (3) The pressure of oxygen seemed to have little effect.

On the basis of his ^{35}S studies, Norris (1950) concluded that the reaction rates were not diffusion limited, but determined by a chemical process. He also felt that the reaction occurred in the liquid phase and involved essentially an oxidation of

sulphur dioxide by sulphuric acid. Since hot sulphuric acid is normally a good oxidizing agent, he expressed surprise at the slow rate of reaction. It is however much faster than the $SO_2 \leftrightarrow SO_3$ gas phase exchange (Voge, 1939). The latter is strongly catalyzed by water (Voge, 1939; Norris, 1950), but the data were irreproducible and the rate-determining step did not appear to be $SO_3 \rightleftharpoons SO_2 + \frac{1}{2} O_2$ (Norris, 1950). This latter observation seems consistent with the ineffectiveness of oxygen pressure upon the exchange rate in the present study. Further, since exchange in the present study proceeded at a reasonable rate in the Na_2SO_4 solution (and also occurred with solid Na_2SO_4 i.e., no liquid phase), one questions the effectiveness of the concentrated sulphuric acid. The results of Norris (1950) and the present work raise numerous questions about the mechanism.

In any case, exchange does occur between SO_2 and sulphate and the effects are considerable. There are at least two sites in nature where such exchange might be identified.

(1) eruption of undersea volcanoes which would place volcanic gases in contact with seawater sulphate.

(2) atmospheric precipitation where SO_2 from industrial combustion dissolves in rainwater and undergoes oxidation in solution to sulphate.

$NaHSO_3 \leftrightarrow SO_2$ EXCHANGE:

In the present experiments, the equilibrium exchange for the reaction

$$Na\ H^{32}SO_3(sol'n) + {}^{34}SO_2\ (gas) \underset{}{\overset{K}{\rightleftharpoons}} Na\ H^{34}SO_3\ (sol'n) + {}^{32}SO_2\ (gas)$$

was found to be 1.012 at 21°C and 1.008 at 80°C. Thode et al (1945) reported this exchange constant to be 1.019 $\pm$ 0.002 at 25°C. It is interesting that Urey et al (1937) and Stewart and Cohen (1940) reported the value of K for this exchange at room temperature to be 1.012. This value was based on transport data in the separation of sulphur isotopes by chemical exchange. It was assumed that the transport of the heavier isotope remained constant and was proportional to K. Cohen (1940) however pointed out that the transport was not constant and the factor (K-1) should be 50 to 100% higher than that measured from transport data. Therefore, the results of Thode et al (1945) are consistent with Cohen's suggestion and it would seem that the K values of the present experiments are low. Experimental details are lacking in the publication by Thode et al (1945) and it may be that differences in the experimental procedure might account for the discrepancy. In the present experiment, an attempt was not made to assess the $^{34}S/^{32}S$ composition of bisulphite

in solution at the end of the experiment. If there had been some dissociation phenomena, then SO_2 may have been equilibrating with more than one species and this may account for the differences in the two studies.

EXCHANGE OF H_2S WITH THIOSULPHATE SOLUTION:

EXCHANGE OF SO_2 WITH THIOSULPHATE SOLUTION:

These studies will be discussed together since they have some features in common. It is seen that in both cases, the experiments were complicated by the precipitation of sulphur and one has the problem of determining its origin. The most likely source is the decomposition of thiosulphate

$$S_2O_3^{=} \rightleftharpoons S + SO_3^{=}$$

Agarwala et al (1965) studied the kinetic isotope effects in the decomposition of $S_2O_3^{=}$ and found that the sulphur produced was depleted in ^{34}S by 19 δ-units while the corresponding sulphite was depleted in ^{34}S by 9 δ-units. Since the isotope effects were appreciable, it was clear that S-S bonds ruptured in the rate-determining step of the reaction. They concluded that the isotope effects were not consistent with the proposed mechanisms of La Mer and Davis and postulated a simple bimolecular three-centred reaction.

In the present experiments, the $^{34}S/^{32}S$ composition of the ligand S-atom was determined to be +9.9‰. Therefore, if the sulphur was formed entirely from the decomposition of thiosulphate, its ^{34}S value would range from about -10‰ for a small percentage decomposition (due to the kinetic isotope effect of 19‰) through to +9.9‰ at 100 percent decomposition (all of the ligand sulphur would become elemental sulphur).

If this precipitated sulphur did not exchange, then its isotopic composition should be consistent irregardless of whether SO_2 or H_2S was equilibrated. It was found however that the sulphur differed in both cases. For the H_2S studies ($\delta^{34}S$ of H_2S = +22.6‰ initially) the precipitated sulphur had the values +10.7, +10.7, and +13.4‰ at the three temperatures studied (80°C, 60°C, 21°C). In the case of SO_2, ($\delta^{34}S$ of SO_2 = +1.4‰ initially), the sulphur produced had an isotopic composition of -0.5‰. The amount of sulphur precipitated corresponded to the following percentages of the initial ligand sulphur

H_2S equilibrations; 5% at 21°C, 3% at 60°C, and 2% at 80°C: Equilibration with SO_2; 1% at 21°C. Therefore if the sulphur resulted from simple thiosulphate dissociation, its isotopic composition should have been about -10‰. Therefore, it is clear that more than simple dissociation is involved. One wonders why less sulphur

is precipitated with increasing temperature in the H_2S equilibration experiments. There is also the question of whether it is more than coincidence that the H_2S achieves a final value close to that of the ligand sulphur, i.e., could the H_2S somehow have been produced from ligand sulphur by a mechanism in which the S-S bond rupture in the thiosulphate was not rate controlling and so no isotope effect occurred? Voge (1939) found that the exchange using $H_2{}^{35}S$ was essentially complete in 24 hours at 100°C. The exchange is designated

$$H^{35}S^- + SSO_3^= \rightleftharpoons HS^- + {}^{35}SSO_3^=$$

since there is not noticeable exchange between the ligand and central sulphur atom. From the analogous mechanism for oxygen exchange between OH^- and PO_4^{3-}, Voge (1939) suggested that the exchange may depend on the reactions

$$S_2O_3^= \rightleftharpoons S + SO_3^=$$

$$S + S^= \rightleftharpoons S_2^=$$

Voge found that exchange between sulphur atoms in polysulfide ion readily occurred. In fact, colour changes noted in the yellow precipitate of the present experiments may have been due to varying mixtures of polysulphides and sulphur. It is interesting that Voge also reported a light yellow colour in his solutions but found it to

be due to iron in the glass.

The present results cannot elucidate the mechanisms. Ames and Willard (1951) studied the kinetics of exchange between thiosulphate and sulphite. They found that the ligand sulphur transferred to $SO_3^=$ in the range 60° to 100°C and the rate was proportional to the sulphite concentration and also to the thiosulphate concentration. Evidence indicated that the equilibrium of thiosulphate with sulphur and sulphite was not a part of the sulphur transfer mechanism. Since sulphite and thiosulphate ions may exist in a variety of states of hydration and ion pair formation in aqueous solution, these authors suggested that the exchange might proceed through one of the less predominant of these forms.

The present experimental approach could be more informative if thiosulphate of differing $^{34}S/^{32}S$ ratios in the ligand and central sulphur atoms were used. This might clarify the origin of the precipitated sulphur and answer the question of whether the H_2S achieves the $^{34}S/^{32}S$ composition of the ligand. This approach may also reveal why the SO_2 becomes so enriched in ^{32}S.

EXCHANGE BETWEEN H_2SO_4 AND H_2S:

Voge (1939) found that the exchange between sulphide and sulphate in alkaline solution was not appreciable at 110°C after 36 hours. It was interesting to study

this exchange because it involves the highest and lowest valence states of sulphur in nature and sulphate is often found co-existing with sulphide. Our experiments however, were complicated by the disappearance of H_2S and the formation of sulphur and SO_2. The isotope behavior is as follows: H_2SO_4 (-0.6‰) and H_2S (+22.6‰) have somehow reacted to produce elemental sulphur (+19.2‰) and SO_2 (-18.5‰). Since the sulphur is nearly the same composition as the H_2S, it would seem that it was formed from the H_2S by oxidation and did not undergo further processes. This is supported by two arguments (1) In the studies with sulphur powder, to be discussed, no noticeable alteration to the $^{34}S/^{32}S$ abundance occurred and (2) If the sulphur had exchanged with the H_2SO_4 it should have become significantly depleted in ^{34}S (see Table I, page 33). The SO_2 on the other hand is severely depleted in ^{34}S. From the other studies in this thesis, it would seem unreasonable to attribute the isotopic composition of the SO_2 to exchange with H_2SO_4 for two reasons; (1) The exchange with H_2SO_4 at room temperature is very slow in comparison to the duration of the present experiment (2) If exchange had occurred, the SO_2 should have been even more depleted in ^{34}S (about -35‰). One explanation is as follows; the SO_2 may have been formed from the H_2SO_4. This would involve S-O bond rupture with an

attending kinetic isotope effect. In the reactions

$$^{32}SO_4 = \overset{k_1}{\rightarrow} H_2{}^{32}S \text{ and } {}^{34}SO_4 = \overset{k_2}{\rightarrow} H_2{}^{34}S,$$

Harrison and Thode (1957) found k_1/k_2 to be 1.022 and identified the isotope fractionation with the initial S-O bond rupture. In the present experiment, the isotopic composition of the SO_2 (-18.5‰) seems consistent with this kinetic isotope effect. It would be interesting to (1) examine the conversion of H_2S near the beginning of the reaction and (2) repeat the experiments with dilute sulphate solutions and even solid sulphate. If the latter cases behaved similarly to the present studies, there would be a number of terrestrial implications since sulphide is often found in contact with sulphate.

EXCHANGES WITH ELEMENTAL SULPHUR:

In all cases examined, there was no significant alteration to the $^{34}S/^{32}S$ composition of the sulphur. Variations noted in Table XXVIII can be explained entirely by difficulties experienced in separating solution from the sulphur powder. The results do not rule out the possibility of some exchange* between sulphur and the ions

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* It is interesting that Rees (Ph.D. Thesis, Physics Department, McMaster University, 1964) found that exchange occurred between amorphous Se and $SeO_3^=$ solution.

in solution. Exchange may have occurred on the surface, but no exchange occurred between the interior and surface sulphur atoms. This could be verified by examing the isotopic composition of the ions in solution as a function of time.

The results suggest that when sulphur has once formed, its isotopic composition is not significantly altered at low temperatures. This has terrestrial significance in the Cyrenaican Lake and salt dome studies discussed in Chapter II.

SUMMARY

In this thesis, it is seen that a number of chemical reactions with sulphur may lead to significant alterations of the $^{34}S/^{32}S$ abundance. Some of the cases studied were true isotope exchange reactions while others were complicated by side reactions. A number of the reactions studied have relevance to natural $^{34}S/^{32}S$ fractionation processes. The purpose of this summary is to outline explicitly the contributions which the author has made to the whole problem of sulphur isotope exchange.

The overall approach to the problem is a contribution in itself. Exchange times have been derived by monitoring the $^{34}S/^{32}S$ abundance of participating sulphur molecules with time, whereas all previous data were based on ^{35}S studies. The partial exchange technique of Northrop and Clayton (1966) was applied for the first time to sulphur isotope exchange studies. This permitted an estimation of the isotopic equilibrium exchange constant K for cases where near equilibrium conditions were not attained.

More specific contributions are now summarized.

In the $H_2SO_4 \leftrightarrow SO_2$ exchange system;

1) Data for rate of exchange and K values were extended to lower temperatures (longer exchange times) than had been previously reported using ^{35}S or stable isotope techniques.

2) The dependence of exchange rate upon the concentration of SO_2 and O_2 was examined. It was shown that the exchange rate was proportional to the SO_2 pressure whereas other authors (eg. Norris, 1950) have assumed this. It was also shown that O_2 seems ineffective in influencing the exchange rate and this seems consistent with other observations reported by Norris (1950) and discussed on page 118 of this thesis.

The exchange of SO_2 with solid Na_2SO_4 and Na_2SO_4 in solution is not only interesting because the author found that it occurred, but it also sheds light on the $H_2SO_4 \leftrightarrow SO_2$ exchange. It would appear that concentrated H_2SO_4 is not as effective as one would expect by virtue of its oxidizing capabilities.

The exchange between H_2S and H_2SO_4 was found to be so slow as to be almost immeasureable in previous studies. This system was examined in this thesis because of its relevance to natural variations. Although direct exchange was not observed, the production of SO_2 and elemental sulphur proved extremely interesting. The SO_2 was depleted by 18.5 ‰ in ^{34}S and this is tentatively identified with a kinetic isotope effect in S-O bond rupture during reduction of the H_2SO_4. Therefore, despite the fact that knowledge concerning the exchange capabilities of this system was not obtained, nevertheless significant

isotope fractionation was found.

Isotope fractionation during the interaction of H_2S or SO_2 with thiosulphate is reported for the first time in this thesis. It is clear that significant isotope fractionation arises, but the mechanisms are very involved as discussed on pages 120 - 123.

The isotopic composition of sulphur powder was not altered extensively while in contact with various sulphur-containing ions in aqueous solution.

In the $H_2SO_4 \leftrightarrow SO_2$ equilibrations, the results were found to be consistent with those of Dunford et al (1957). On the other hand, the exchange between HSO_3^- and SO_2 gave smaller values of K than previously reported (Thode et al, 1945). It would seem that this latter discrepancy is due to a chemical difference between the two studies.

The mechanisms of all of the systems studied in this thesis are complex. However, it would seem that the techniques employed could be productive in elucidating the mechanisms if the following procedures are followed:

(1) The system should be studied under a variety of conditions to see what role is played by the participating species.

(2) Reactants of widely differing isotopic composition should be used in replicate experiments. In the case of exchange between SO_2 or H_2S and thiosulphate, the source

of the precipitated sulphur could be ascertained if this procedure was followed. The side reactions which occurred in other systems studied could also be characterized.

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A P P E N D I X

C A L C U L A T I O N S

Tables V-(a) to XXV-(a)

Table V-(a)

Series A

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 2h:-						
-1.0	0.9996	-0.1	- 7.6	0.9930	-3.1	-3.0
-3.5	0.9971	-1.3	- 8.3	0.9923	-3.4	-2.1
-7.5	0.9931	-3.1	- 9.9	0.9907	-4.1	-1.0
-8.9	0.9917	-3.6	-10.4	0.9902	-4.3	-0.7
-10.4	0.9902	-4.3	-10.7	0.9899	-4.4	-0.1
Δt = 4h:-						
-1.0	0.9996	-0.1	- 9.9	0.9907	-4.1	-4.0
-3.5	0.9971	-1.3	-10.2	0.9904	-4.2	-2.9
-5.2	0.9954	-2.0	-10.4	0.9902	-4.3	-2.3
-8.9	0.9917	-3.6	-10.7	0.9899	-4.4	-0.8
-9.5	0.9911	-3.9	-10.7	0.9899	-4.4	-0.5
Δt = 6h:-						
-1.0	0.9996	-0.1	-10.6	0.9900	-4.4	-4.3
-3.5	0.9971	-1.3	-10.7	0.9899	-4.4	-3.1
-8.9	0.9917	-3.6	-10.7	0.9899	-4.4	-0.8
-9.5	0.9911	-3.9	-10.7	0.9899	-4.4	-0.5
-9.9	0.9907	-4.1	-10.7	0.9899	-4.4	-0.3

Table VI-(a)

Series B

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 2h:-						
-1.1	0.9995	-0.2	- 9.5	0.9911	-3.8	-3.6
-2.0	0.9986	-0.6	- 9.8	0.9908	-4.1	-3.5
-5.5	0.9951	-2.2	-10.4	0.9902	-4.3	-2.1
-7.6	0.9930	-3.1	-10.9	0.9897	-4.5	-1.4
-9.8	0.9908	-4.1	-11.5	0.9891	-4.8	-0.7
Δt = 4h:-						
-2.0	0.9986	-0.6	-11.5	0.9891	-4.8	-4.2
-5.5	0.9951	-2.2	-11.6	0.9890	-4.8	-2.6
-7.6	0.9930	-3.1	-11.6	0.9890	-4.8	-1.7
-8.9	0.9917	-3.6	-11.6	0.9890	-4.8	-1.2
-9.8	0.9908	-4.1	-11.6	0.9890	-4.8	-0.7
Δt - 6h:-						
-1.1	0.9995	-0.2	-11.6	0.9890	-4.8	-4.6
-2.0	0.9986	-0.6	-11.6	0.9890	-4.8	-9.2
-5.5	0.9951	-2.2	-11.6	0.9890	-4.8	-2.6
-7.0	0.9936	-2.8	-11.6	0.9890	-4.8	-2.0
-8.9	0.9917	-3.6	-11.6	0.9890	-4.8	-1.2

Table VII(a)

Series C

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	1000 x $\ell n \alpha_f$	1000 x $(\ell n \alpha_f - \ell n \alpha_i)$
Δt = 2h:-						
- 1.0	0.9996	-0.1	- 8.9	0.9917	-3.6	-3.5
- 3.0	0.9976	-1.0	- 9.4	0.9912	-3.8	-2.8
- 4.0	0.9967	-1.4	- 9.7	0.9909	-4.0	-2.6
- 6.5	0.9941	-2.6	-10.3	0.9903	-4.3	-1.7
-10.3	0.9903	-4.3	-11.7	0.9889	-4.8	-0.5
Δt = 4h:-						
- 1.0	0.9996	-0.1	-11.2	0.9894	-4.6	-4.5
- 2.1	0.9985	-0.7	-11.3	0.9893	-4.7	-4.0
- 3.0	0.9976	-1.0	-11.4	0.9892	-4.7	-3.7
-6.5	0.9941	-2.6	-11.7	0.9889	-4.8	-2.2
-10.3	0.9903	-4.3	-12.0	0.9886	-4.9	-0.6
Δt = 6h:-						
- 1.0	0.9996	-0.1	-11.9	0.9887	-4.9	-4.9
- 2.1	0.9985	-0.7	-12.0	0.9886	-4.9	-4.2
- 3.0	0.9976	-1.0	-12.0	0.9886	-4.9	-3.9
- 4.0	0.9967	-1.4	-12.0	0.9886	-4.9	-3.5
- 8.9	0.9917	-3.6	-12.0	0.9886	-4.9	-1.3

Table VIII-(a)

Series D

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 2 h:-						
-1.0	0.9996	-0.1	- 9.1	0.9915	-3.7	-3.6
-3.0	0.9976	-1.0	- 9.7	0.9909	-4.0	-3.0
-4.7	0.9959	-1.8	- 9.9	0.9907	-4.1	-2.3
-6.8	0.9938	-2.8	-10.5	0.9901	-4.3	-1.5
-10.5	0.9901	-4.4	-11.7	0.9889	-4.8	-0.4
Δt = 4 h:-						
-1.0	0.9996	-0.1	-11.3	0.9893	-4.7	-4.6
-2.0	0.9986	-0.6	-11.4	0.9892	-4.7	-4.1
-3.0	0.9976	-1.0	-11.5	0.9891	-4.8	-3.8
-6.8	0.9938	-2.8	-11.7	0.9889	-4.8	-2.0
-9.1	0.9915	-3.7	-11.9	0.9887	-4.9	-1.2
Δt = 6 h:-						
-1.0	0.9996	-0.1	-11.9	0.9887	-4.9	-4.8
-2.0	0.9986	-0.6	-11.9	0.9887	-4.9	-4.3
-3.0	0.9976	-1.0	-11.9	0.9887	-4.9	-3.9
-4.0	0.9966	-1.4	-11.9	0.9887	-4.9	-3.5
-6.0	0.9946	-2.3	-11.9	0.9887	-4.9	-2.6

Table IX-(a)

Series - E

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 2 h:-						
-1.2	0.9994	-0.2	- 9.2	0.9914	-3.7	-3.5
-2.0	0.9986	-0.6	- 9.6	0.9910	-3.9	-3.3
-4.4	0.9962	-1.6	-10.3	0.9903	-4.3	-2.7
-6.0	0.9946	-2.3	-10.7	0.9899	-4.4	-2.1
-9.9	0.9907	-4.1	-11.8	0.9888	-4.8	-0.7
Δt = 4 h:-						
-1.2	0.9994	-0.2	-11.7	0.9889	-4.8	-4.6
-2.0	0.9986	-0.6	-11.8	0.9888	-4.9	-4.2
-4.3	0.9963	-1.6	-11.8	0.9888	-4.8	-3.2
-6.0	0.9946	-2.3	-11.9	0.9887	-4.9	-2.6
-9.9	0.9907	-4.1	-11.9	0.9887	-4.9	-0.8
Δt = 6 h:-						
-1.2	0.9994	-0.2	-11.8	0.9888	-4.8	-4.6
-2.0	0.9986	-0.6	-11.9	0.9887	-4.9	-4.3
-4.3	0.9963	-1.6	-11.9	0.9887	-4.9	-3.3
-6.0	0.9946	-2.3	-11.9	0.9887	-4.9	-2.6
-9.9	0.9907	-4.1	-11.9	0.9887	-4.9	-0.8

Table X-(a)

Series P

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 4 h:-						
- 1.0	0.9996	-0.1	-11.3	0.9893	-4.7	-4.6
- 2.0	0.9986	-0.6	-11.4	0.9892	-4.7	-4.1
- 5.0	0.9956	-1.9	-11.5	0.9891	-4.8	-2.9
- 6.1	0.9945	-2.4	-11.7	0.9889	-4.8	-2.4
-12.0	0.9886	-4.9	-12.4	0.9882	-5.1	-0.2
Δt = 2 h:-						
- 1.0	0.9996	-0.1	- 9.8	0.9908	-4.0	-3.9
- 2.0	0.9986	-0.6	-10.4	0.9902	-4.3	-3.7
- 5.0	0.9956	-1.9	-10.8	0.9898	-4.4	-2.5
- 6.1	0.9945	-2.4	-11.0	0.9896	-4.5	-2.1
-12.0	0.9886	-4.9	-12.3	0.9883	-5.1	-0.2
Δt = 6 h:-						
- 1.0	0.9996	-0.1	-11.8	0.9888	-4.4	-4.3
- 2.0	0.9986	-0.6	-11.9	0.9887	-4.9	-4.3
- 5.0	0.9956	-1.9	-12.0	0.9886	-4.9	-3.0
- 6.1	0.9945	-2.4	-12.1	0.9885	-5.0	-2.6
-12.0	0.9886	-4.9	-12.4	0.9882	-5.1	-0.2

Table XI-(a)

Series - F

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 2 h:-						
- 1.0	0.9996	-0.1	- 6.8	0.9938	-2.8	-2.7
- 3.9	0.9967	-1.4	- 8.05	0.9925	-3.7	-2.3
- 8.7	0.9918	-3.6	-10.6	0.9900	-4.4	-0.8
-10.6	0.9900	-4.4	-11.5	0.9891	-4.8	-0.4
-11.1	0.9895	-4.6	-11.6	0.9890	-4.8	-0.2
Δt = 4 h:-						
- 1.0	0.9996	-0.1	- 9.5	0.9911	-3.9	-3.8
- 2.2	0.9984	-0.7	- 9.8	0.9908	-4.1	-3.4
- 3.9	0.9967	-1.4	-10.2	0.9904	-4.2	-2.8
- 8.1	0.9925	-3.3	-11.3	0.9893	-4.7	-1.4
- 9.8	0.9908	-4.1	-11.6	0.9890	-4.8	-0.7
Δt = 6 h:-						
- 0.5	1.0001	0	-10.9	0.9897	-4.5	-4.5
- 1.0	0.9996	-0.1	-11.0	0.9896	-4.5	-4.4
- 2.2	0.9984	-0.7	-11.1	0.9895	-4.6	-3.9
- 5.3	0.9953	-2.1	-11.5	0.9891	-4.8	-2.7
- 7.3	0.9933	-3.0	-11.6	0.9890	-4.8	-1.8

Table XII-(a)

Series G

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 2 h:-						
- 1.7	0.9989	-0.5	- 7.3	0.9933	-3.0	-2.5
- 3.5	0.9971	-1.3	- 8.1	0.9925	-3.3	-2.0
- 5.1	0.9955	-2.0	- 8.8	0.9918	-3.6	-1.6
- 7.3	0.9933	-3.0	-10.0	0.9906	-4.1	-1.1
-10.0	0.9906	-4.1	-11.5	0.9891	-4.8	-0.7
Δt = 4 h:-						
- 1.0	0.9996	-0.1	-9.8	0.9908	-4.1	-4.0
- 1.7	0.9989	-0.5	-10.0	0.9906	-4.1	-3.6
- 3.1	0.9975	-1.1	-10.4	0.9902	-4.3	-3.2
- 3.5	0.9971	-1.3	-10.5	0.9901	-4.4	-3.1
- 8.1	0.9925	-3.3	-11.7	0.9890	-4.8	-1.5
Δt = 6 h:-						
- 0.2	1.0004	0	-11.3	0.9893	-4.7	-4.7
- 0.6	1.0000	0	-11.3	0.9893	-4.7	-4.7
- 1.0	0.9996	-0.1	-11.4	0.9892	-4.7	-4.6
- 3.9	0.9967	-1.4	-11.8	0.9888	-4.8	-3.4
- 5.1	0.9955	-2.0	-11.9	0.9887	-4.9	-2.9

Table XIII-(a)

Series - H

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 2 h:-						
- 1.0	0.9996	-0.1	- 3.8	0.9968	-1.4	-1.3
- 3.8	0.9968	-1.4	- 6.1	0.9945	-2.4	-1.0
- 6.1	0.9945	-2.4	- 8.0	0.9926	-3.2	-0.8
- 8.0	0.9926	-3.2	- 9.5	0.9911	-3.9	-0.7
-12.0	0.9886	-4.9	-13.0	0.9876	-5.4	-0.5
Δt = 4 h:-						
- 1.0	0.9996	-0.1	- 9.5	0.9911	-3.9	-3.8
- 3.0	0.9976	-1.0	-10.5	0.9901	-4.4	-3.4
- 4.0	0.9966	-1.4	-11.0	0.9896	-4.5	-3.1
- 6.1	0.9945	-2.4	-12.1	0.9885	-5.0	-2.6
-11.0	0.9896	-4.5	-14.3	0.9863	-6.0	-1.5
Δt = 6 h:-						
- 1.0	0.9996	-0.1	-12.1	0.9885	-5.0	-4.9
- 1.5	0.9991	-0.4	-12.3	0.9883	-5.1	-4.7
- 3.0	0.9976	-1.0	-12.8	0.9878	-5.3	-4.3
- 5.0	0.9956	-1.9	-13.5	0.9871	-5.7	-3.8
- 5.9	0.9947	-2.3	-14.4	0.9862	-6.0	-3.7

Table XIV-(a)

Series I

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 2 h:-						
- 0.5	1.0001	0	- 5.1	0.9955	-2.0	-2.0
- 3.0	0.9976	-1.0	- 7.1	0.9935	-2.9	-1.9
- 7.1	0.9935	-2.9	-10.1	0.9905	-4.2	-1.3
-10.6	0.9900	-4.4	-12.5	0.9881	-5.2	-0.8
-13.4	0.9872	-5.6	-14.2	0.9864	-5.9	-0.3
Δt = 4 h:-						
- 0.5	1.0001	0	- 8.7	0.9919	-3.5	-3.5
- 3.0	0.9976	-1.0	-10.1	0.9905	-4.2	-3.2
- 5.1	0.9955	-2.0	-11.2	0.9894	-4.6	-2.6
- 7.1	0.9935	-2.9	-12.1	0.9885	-5.0	-2.1
-11.2	0.9894	-4.6	-13.9	0.9867	-5.8	-1.2
Δt - 6 h:-						
- 0.5	1.0001	0	-11.2	0.9894	-4.6	-4.6
- 3.0	0.9976	-1.0	-12.1	0.9885	-5.0	-4.0
- 4.1	0.9965	-1.5	-12.5	0.9881	-5.2	-3.7
- 5.1	0.9955	-2.0	-12.8	0.9878	-5.3	-3.3
-10.1	0.9905	-4.2	-14.2	0.9864	-5.9	-1.7

Table XV-(a)

Series J

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 2 h:-						
- 1.0	0.9996	-0.1	- 5.6	0.9950	-2.2	-2.1
- 3.5	0.9971	-1.3	- 7.5	0.9931	-3.1	-1.8
- 7.5	0.9931	-3.1	-10.4	0.9902	-4.3	-1.2
-10.4	0.9902	-4.3	-12.5	0.9881	-5.2	-0.9
-13.3	0.9873	-5.6	-14.3	0.9863	-6.0	-0.4
Δt = 4 h:-						
- 1.0	0.9996	-0.1	- 9.1	0.9915	-3.7	-3.6
- 3.5	0.9971	-1.3	-10.4	0.9902	-4.3	-3.0
- 5.6	0.9950	-2.2	-11.6	0.9890	-4.8	-2.6
- 7.5	0.9931	-3.1	-13.6	0.9870	-5.7	-2.6
-12.5	0.9881	-5.2	-14.5	0.9861	-6.1	-0.9
Δt = 6 h:-						
- 1.0	0.9996	-0.1	-11.6	0.9890	-4.8	-4.7
-3.5	0.9971	-1.3	-12.5	0.9881	-5.2	-3.9
- 5.6	0.9950	-2.2	-13.3	0.9873	-5.6	-3.4
- 7.5	0.9931	-3.1	-14.0	0.9866	-5.8	-2.7
- 9.1	0.9915	-3.7	-14.3	0.9863	-6.0	-2.3

Table XVI-(a)

Series O

δ_i	α_i	$1000 \ln\alpha_i$	δ_f	α_f	$1000 \times \ln\alpha_f$	$1000 \times (\ln\alpha_f - \ln\alpha_i)$
Δt = 10 d:-						
- 2.0	0.9986	-0.6	- 5.4	0.9952	-2.1	-1.5
- 4.2	0.9964	-1.5	- 7.4	0.9932	-3.0	-1.5
- 6.4	0.9942	-2.5	- 9.2	0.9914	-3.7	-1.2
-10.0	0.9906	-4.1	-12.2	0.9884	-5.0	-0.9
-15.4	0.9852	-6.5	-16.2	0.9844	-6.8	-0.3
Δt = 20 d:-						
- 2.0	0.9986	-0.6	- 8.4	0.9922	-3.4	-2.8
- 4.2	0.9964	-1.5	-10.0	0.9906	-4.1	-2.6
- 6.4	0.9942	-2.5	-11.6	0.9890	-4.8	-2.3
-14.4	0.9862	-6.0	-16.2	0.9844	-6.8	-0.8
-16.2	0.9844	-6.8	-17.4	0.9832	-7.3	-0.5
Δt = 30 d:-						
- 2.0	0.9986	-0.6	-11.0	0.9896	-4.5	-3.9
- 6.4	0.9942	-2.5	-13.4	0.9872	-5.6	-3.1
- 7.4	0.9932	-3.0	-13.8	0.9868	-5.7	-2.7
-10.0	0.9906	-4.1	-15.0	0.9856	-6.3	-2.2
-15.4	0.9852	-6.5	-17.4	0.9832	-7.3	-0.8

Table XVII-(a)

Series V

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	1000 x $\ell n \alpha_f$	1000 x $(\ell n \alpha_f - \ell n \alpha_i)$
Δt = 10 d:-						
+1.5	1.0021	+0.8	-1.9	0.9988	-0.6	-1.4
+1.0	1.0016	+0.6	-2.2	0.9984	-0.7	-1.3
-0.5	1.0001	+0.4	-2.4	0.9982	-0.8	-1.2
-2.4	0.9982	-0.8	-3.1	0.9976	-1.0	-0.2
-3.6	0.9970	-1.3	-3.7	0.9969	-1.3	0.0
Δt = 20 d:-						
+1.5	1.0021	+0.8	-2.8	0.9978	-1.0	-1.8
+1.0	1.0016	+0.6	-2.9	0.9977	-1.0	-1.6
-2.4	0.9982	-0.8	-3.4	0.9972	-1.2	-0.4
-3.4	0.9972	-1.2	-3.7	0.9969	-1.3	-0.1
-3.9	0.9967	-1.4	-4.1	0.9965	-1.5	-0.1
Δt = 30 d:-						
+1.5	1.0021	+0.8	-3.3	0.9974	-1.1	-1.9
+1.0	1.0016	+0.6	-3.4	0.9973	-1.2	-1.8
-2.4	0.9982	-0.8	-3.5	0.9972	-1.2	-0.4
-3.4	0.9972	-1.2	-3.8	0.9969	-1.3	-0.1
-3.8	0.9969	-1.3	-4.1	0.9965	-1.5	-0.2

Table XIX (a)

Series Q

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 10 d:-						
+1.0	0.9925	-3.3	-0.2	0.9907	-4.1	-0.8
+0.6	0.9921	-3.5	-0.5	0.9910	-3.9	-0.4
-0.5	0.9910	-3.9	-1.1	0.9904	-4.2	-0.3
-1.1	0.9904	-4.2	-1.5	0.9900	-4.4	-0.2
-1.6	0.9899	-4.4	-1.8	0.9897	04.5	-0.1
Δt = 20 d:-						
+1.0	0.9925	-3.3	-1.0	0.9905	-4.2	-0.9
+0.6	0.9921	-3.5	-1.1	0.9910	-3.9	-0.4
-0.5	0.9910	-3.9	-1.5	0.9900	-4.4	-0.5
-1.1	0.9904	-4.2	-1.7	0.9898	-4.4	-0.2
-1.6	0.9899	-4.4	-1.9	0.9896	-4.5	-0.1
Δt = 30 d:-						
+1.0	0.9925	-3.3	-1.4	0.9901	-4.4	-1.1
+0.6	0.9921	-3.5	-1.5	0.9900	-4.4	-0.9
-0.5	0.9910	-3.9	-1.7	0.9898	-4.4	-0.5
-1.1	0.9904	-4.2	-1.9	0.9896	-4.5	-0.3
-1.6	0.9899	-4.4	-2.0	0.9895	-4.6	-0.2

Table XX-(a)

Series M

δ_i	α_i	$1000 \ln\alpha_i$	δ_f	α_f	$1000 \times \ln\alpha_f$	$1000 \times (\ln\alpha_f - \ln\alpha_i)$
Δt = 1 h:-						
-1.0	0.9962	-1.6	-3.7	0.9935	-2.9	-1.3
-1.8	0.9954	-2.0	-4.0	0.9932	-3.0	-1.0
-3.1	0.9941	-2.6	-4.5	0.9927	-3.2	-0.6
-4.0	0.9932	-3.0	-4.8	0.9924	-3.3	-0.3
-4.5	0.9927	-3.2	-4.8	0.9924	-3.3	-0.3
-4.5	0.9927	-3.2	-4.8	0.9924	-3.3	-0.1
Δt = 2 h:-						
-1.0	0.9962	-1.6	-4.7	0.9925	-3.3	-1.7
-1.8	0.9954	-2.0	-4.8	0.9924	-3.3	-1.3
-3.1	0.9941	-2.6	-4.8	0.9924	-3.3	-0.7
-4.0	0.9932	-3.0	-4.8	0.9924	-3.3	-0.3
-4.5	0.9927	-3.2	-4.8	0.9924	-3.3	-0.1
Δt = 4 h:-						
-1.0	0.9962	-1.6	-4.8	0.9924	-3.3	-1.7
-1.8	0.9954	-2.0	-4.8	0.9924	-3.3	-1.3
-3.1	0.9941	-2.6	-4.8	0.9924	-3.3	-0.7
-4.0	0.9932	-3.0	-4.8	0.9924	-3.3	-0.3
-4.8	0.9924	-3.3	-4.9	0.9923	-3.4	-0.1

Table XXI-(a)

Series N

δ_i	α_i	$1000 \ln\alpha_i$	δ_f	α_f	$1000 \times \ln\alpha_f$	$1000 \times (\ln\alpha_f - \ln\alpha_i)$
Δt = 1 h:-						
-1.0	0.9962	-1.6	-4.4	0.9928	-3.1	-1.5
-2.0	0.9952	-2.1	-4.8	0.9924	-3.3	-1.2
-2.5	0.9947	-2.3	-5.0	0.9922	-3.4	-1.1
-3.9	0.9933	-3.0	-5.7	0.9915	-3.7	-0.7
-5.7	0.9915	-3.7	-6.7	0.9905	-4.2	-0.5
-6.7	0.9905	-4.2	-7.4	0.9898	-4.4	-0.2
Δt = 2 h:-						
-1.0	0.9962	-1.6	-5.9	0.9913	-3.8	-2.2
-2.0	0.9952	-2.1	-6.2	0.9910	-3.9	-1.8
-3.9	0.9933	-3.0	-6.7	0.9905	-4.2	-1.2
-5.0	0.9922	-3.4	-7.1	0.9901	-4.4	-1.0
-7.4	0.9898	-4.4	-7.9	0.9893	-4.7	-0.3
Δt = 4 h:-						
-1.0	0.9962	-1.6	-7.5	0.9897	-4.5	-2.9
-2.0	0.9952	-2.1	-7.6	0.9896	-4.5	-2.4
-3.9	0.9933	-3.0	-7.8	0.9894	-4.6	-1.6
-4.4	0.9928	-3.1	-7.8	0.9894	-4.6	-1.5
-5.0	0.9922	-3.4	-7.9	0.9893	-4.7	-1.3

Table XXII-(a)

Series R

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 1 h:-						
-1.5	0.9885	-5.0	- 6.8	0.9833	-7.3	-2.3
-4.0	0.9860	-6.1	- 7.5	0.9826	-7.6	-1.5
-5.5	0.9846	-6.7	- 8.3	0.9819	-7.9	-1.2
-7.5	0.9826	-7.6	- 9.5	0.9806	-8.5	-0.9
-9.5	0.9806	-8.5	-10.8	0.9793	-9.1	-0.6
Δt = 2 h:-						
-1.5	0.9885	-5.0	- 9.0	0.9811	-8.2	-3.2
-4.0	0.9860	-6.1	- 9.5	0.9806	-8.5	-2.4
-5.5	0.9846	-6.7	-10.0	0.9801	-8.8	-2.1
-6.8	0.9833	-7.3	-10.5	0.9796	-8.9	-1.6
-9.5	0.9806	-8.5	-11.7	0.9784	-9.5	-1.0
Δt = 4 h:-						
-1.5	0.9885	-5.0	-11.0	0.9791	-9.2	-4.2
-4.0	0.9860	-6.1	-11.7	0.9784	-9.5	-3.4
-5.5	0.9846	-6.7	-11.9	0.9782	-9.6	-2.9
-6.0	0.9841	-7.0	-12.0	0.9781	-9.7	-2.7
-6.8	0.9833	-7.3	-12.1	0.9780	-9.7	-2.4
-7.5	0.9826	-7.6	-12.3	0.9778	-9.7	-2.1

Table XXIII-(a)

Series S

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	1000 x $\ell n \alpha_f$	1000 x ($\ell n \alpha_f - \ell n \alpha_i$)
Δt = 2 d:-						
+24.0	1.0138	+6.0	+15.6	1.0054	+2.1	-3.9
+23.0	1.0128	+5.5	+15.4	1.0052	+2.1	-3.4
+20.0	1.0098	+4.3	+14.4	1.0043	+1.7	-2.6
+16.6	1.0064	+2.5	+12.8	1.0027	+1.2	-1.3
+12.2	1.0021	+0.8	+10.3	1.0002	0.0	-0.8
Δt = 4 d:-						
+24.0	1.0138	+6.0	+12.3	1.0022	+0.8	-5.2
+23.0	1.0128	+5.5	+12.2	1.0021	+0.8	-4.7
+20.0	1.0098	+4.3	+11.6	1.0015	+0.8	-3.5
+16.6	1.0064	+2.5	+10.7	1.0006	+0.4	-2.1
+14.4	1.0043	+1.7	+10.0	0.9999	0.0	-1.7
Δt = 6 d:-						
+24.0	1.0138	+6.0	+10.4	1.0003	0.0	-6.0
+23.0	1.0128	+5.5	+10.3	1.0002	0.0	-5.5
+20.0	1.0098	+4.3	+10.0	0.9999	0.0	-4.3
+16.6	1.0064	+2.5	+ 9.6	0.9995	-0.2	-2.7
+14.4	1.0021	+1.7	+ 9.3	0.9992	-0.3	-2.0

Table XXIV-(a)

Series U

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 1 d:-						
+19.2	1.0090	+3.7	+14.4	1.0043	+1.7	-2.0
+17.8	1.0076	+3.3	+14.0	1.0039	+1.7	-1.6
+15.0	1.0049	+2.1	+12.7	1.0026	+1.2	-0.9
+14.0	1.0039	+1.7	+12.1	1.0020	+0.8	-0.9
+12.7	1.0026	+1.2	+11.5	1.0014	+0.4	-0.8
Δt = 2 d:-						
+19.2	1.0090	+3.7	+12.4	1.0023	+0.8	-2.9
+17.8	1.0076	+3.3	+12.1	1.0020	+0.8	-2.5
+15.0	1.0049	+2.1	+11.5	1.0014	+0.4	-1.7
+14.0	1.0039	+1.7	+11.2	1.0011	+0.4	-1.3
+12.7	1.0026	+1.2	+11.0	1.0009	+0.4	-0.8
Δt = 4 d:-						
+19.2	1.0090	+3.7	+11.0	1.0009	+0.4	-3.3
+17.8	1.0076	+3.3	+11.0	1.0009	+0.4	-2.9
+15.0	1.0049	+2.1	+11.0	1.0009	+0.4	-1.7
+14.0	1.0039	+1.7	+11.0	1.0009	+0.4	-1.3
+12.7	1.0026	+1.2	+11.0	1.0009	+0.4	-0.8

Table XXV-(a)

Series T

δ_i	α_i	$1000 \ell n \alpha_i$	δ_f	α_f	$1000 \times \ell n \alpha_f$	$1000 \times (\ell n \alpha_f - \ell n \alpha_i)$
Δt = 1 d:-						
+18.0	1.0078	+3.3	+11.6	1.0015	+0.8	-2.5
+15.8	1.0056	+2.5	+10.9	1.0008	+0.4	-2.1
+14.8	1.0047	+2.1	+10.5	1.0004	0.0	-2.1
+13.3	1.0032	+1.2	+ 9.9	0.9998	-0.1	-1.3
+ 9.9	0.9998	-0.1	+ 8.3	0.9982	-0.8	-0.7
Δt = 2 d:-						
+18.0	1.0078	+3.3	+ 9.2	0.9991	-0.4	-3.7
+15.8	1.0056	+2.5	+ 8.8	0.9987	-0.6	-3.1
+14.8	1.0047	+2.1	+ 8.6	0.9985	-0.7	-2.8
+13.3	1.0032	+1.2	+ 8.3	0.9982	-0.8	-3.0
+10.5	1.0004	+0.4	+ 8.0	0.9979	-1.9	-2.3
Δt = 4 d:-						
+18.0	1.0078	+3.3	+ 8.0	0.9979	-1.9	-5.2
+15.8	1.0056	+2.5	+ 8.0	0.9979	-1.9	-4.4
+14.8	1.0047	+2.1	+ 8.0	0.9979	-1.9	-4.0
+13.3	1.0032	+1.2	+ 8.0	0.9979	-1.9	-3.1
+10.5	1.0004	+0.4	+ 8.0	0.9979	-1.9	-2.3

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